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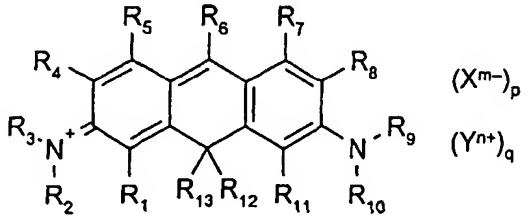
(54) Title: FAST-WRITABLE AND PRECISION-WRITABLE HIGH-CAPACITY OPTICAL STORAGE MEDIA



(I)

(57) Abstract: The invention relates to an optical recording medium, comprising a substrate and a recording layer, wherein the recording layer comprises a compound of formula (I), wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9,R_{10}, R_{11}, R_{12} and R_{13} are each independently of the others hydrogen, G_1 or C_1-C_{24}alkyl, C_2-C_{24}alkenyl, C_2-C_{24}alkynyl, C_3-C_{24}cycloalkyl, C_3-C_{24}cycloalkenyl, C_7-C_{24}aralkyl, C_6-C_{24}aryl, C_4-C_{12}heteroaryl or C_1-C_{12}heterocycloalkyl, each unsubstituted or substituted by one or more identical or different substituents G_1, wherein R_1 and R_2, R_1 and R_{13}, R_2 and R_3, R_3 and R_4, R_4 and R_5, R_5 and R_6, R_6 and R_7, R_7 and R_8, R_8 and R_9, R_9 and R_{10}, R_{10} and R11, R_{11} and R_{12} and/or R_{12} and R_{13} can independently of one another be bonded to one another in pairs separately or, when they contain substitutable sites, *via* a direct bond or *via* a -CH_2-, -O-, -S-, -NH- or -NC_1-C_{24}alkyl-bridge in such a manner that, together with the atoms and bonds indicated in formula (I), five- or six-membered, saturated, unsaturated or aromatic, unsubstituted or G_1-substituted rings are formed, G_1 is any desired substituent,? $_x$m-¿ is an inorganic, organic or organometallic anion, Y^{n+} is a proton or a metal, ammonium or phosphonium cation, and m and n are each independently of the other a number from 1 to 5, and p and q are each independently of the other O or a number from 0.2 to 6, the ratio of p and q to one another, depending upon m and n and, as applicable, the number of charged G_1, being such that in formula (I) there is no excess positive or negative charge. Generally the optical recording medium according to the invention additionally comprises a reflecting layer. The recording media according to the invention exhibit high sensitivity and good playback characteristics, especially at high recording and playback speeds. The light stability is also excellent.

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Fast-writable and precision-writable high-capacity optical storage media

The field of the invention is the optical storage of information on write-once storage media, the information pits being differentiated by the different optical properties of a colorant at written and unwritten sites. This technology is usually termed "WORM" (for example "CD-R" or "DVD-R"); those terms have been retained herein.

Compact discs that are writable at a wavelength of from 770 to 830 nm are known from "Optical Data Storage 1989", Technical Digest Series, Vol. 1, 45 (1989). They are read at a reduced readout power. According to the Orange Book Standard, at the recording wavelength the medium must have a base reflectivity of 65% or more. As recording media it is possible to use, for example, cyanine dyes (JP-58/125246), phthalocyanines (EP-A-676 751, EP-A-712 904), azo dyes (US-5 441 844), double salts (US-4 626 496), dithioethene metal complexes (JP-A-63/288785, JP-A-63/288786), azo metal complexes (US-5 272 047, US-5 294 471, EP-A-649 133, EP-A-649 880) or mixtures thereof (EP-A-649 884).

By using more recent compact high-performance red diode lasers that emit in the range of from 600 to 700 nm it is possible in principle to achieve a 6- to 8-fold improvement in data packing density, in that the track spacing (distance between two turns of the information track) and the size of the pits as well as the redundancy can each be reduced to approximately half the value in comparison with conventional CDs.

This imposes extraordinarily high demands on the recording layer to be used, however, such as high refractive index, high light stability in daylight and under laser radiation of low power density (readout) with, at the same time, high sensitivity under laser radiation of high power density (writing), uniformity of script width at different length pulse durations and also high contrast. The known recording layers still do not possess these properties to an entirely satisfactory extent.

EP-A-0 805 441 describes an optical recording medium comprising xanthene dyes, which can be both recorded and read at from 600 to 700 nm. In the Examples, good results are achieved with a 10 mW laser diode of wavelength

635 nm. It has been found, however, that under practical conditions the results for the dyes disclosed in EP-A-0 805 441 are not able fully to satisfy the demands (which have increased in the interim) in respect of sensitivity, recording speed and mark accuracy and reproducibility, especially in the range from 640 to 680 nm.

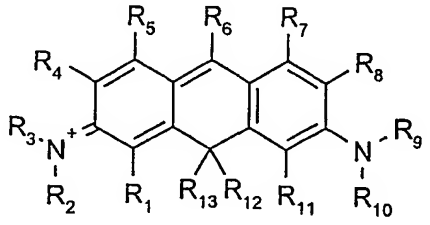
US-3 781 711 discloses laser dye compositions comprising dyes having a rigid structure, including 9,9-dimethyl-2-dimethylamino-7H,9H-anthracene-7-dimethyliminium nitrate. Such compounds are used in high dilution.

WO-A-00/64986 describes carbopyronine fluorescent dyes and their use as marker groups in diagnostics. The absorption maxima and the fluorescent yield are not appreciably altered by coupling such compounds to carriers and biomolecules.

The aim of the invention is to provide an optical recording medium, the recording layer of which has high storage capacity combined with excellent other properties. The recording medium should be both writable and readable, with a minimum of errors, at the same wavelength in the range of from 600 to 700 nm (preferably from 630 to 690 nm) at high speed.

Very surprisingly, by the use of certain carbopyronine dyes as recording layer it has been possible to provide an optical recording medium having properties that are astonishingly better than those of recording media known hitherto.

The invention accordingly relates to an optical recording medium comprising a substrate and a recording layer, wherein the recording layer comprises a compound of formula (I)



(I)

wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12} and R_{13} are each independently of the others hydrogen, G_1, or C_1-C_{24}alkyl, C_2-C_{24}alkenyl,

C_2-C_{24}alkynyl, C_3-C_{24}cycloalkyl, C_3-C_{24}cycloalkenyl, C_7-C_{24}aralkyl, C_6-C_{24}aryl, C_4-C_{12}heteroaryl or C_1-C_{12}heterocycloalkyl, each unsubstituted or substituted by one or more identical or different substituents G_1,

wherein R_1 and R_2, R_1 and R_{13}, R_2 and R_3, R_3 and R_4, R_4 and R_5, R_5 and R_6, R_6 and R_7, R_7 and R_8, R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, R_{11} and R_{12} and/or R_{12} and R_{13} can independently of one another be bonded to one another in pairs separately or, when they contain substitutable sites, *via* a direct bond or *via* a $-CH_2-$, $-O-$, $-S-$, $-NH-$ or $-NC_1$-C_{24}alkyl- bridge in such a manner that, together with the atoms and bonds indicated in formula (I), five- or six-membered, saturated, unsaturated or aromatic, unsubstituted or G_1-substituted rings are formed,

G_1 is any desired substituent,

X^{m-} is an inorganic, organic or organometallic anion,

Y^{n+} is a proton or a metal, ammonium or phosphonium cation, and

m and n are each independently of the other a number from 1 to 5, and p and q are each independently of the other 0 or a number from 0.2 to 6, the ratio of p and q to one another, depending upon m and n and, as applicable, the number of charged G_1 substituents, being such that in formula (I) there is no excess positive or negative charge.

Generally the optical recording medium according to the invention additionally comprises a reflecting layer, but this is not absolutely necessary *per se* and it can be omitted depending upon the type of detector.

Each G_1 is, where applicable independently of any other G_1, any desired substituent, for example halogen, -OH, $-O^-$, -OA, =O, -SH, $-S^-$, -SA, =S, $-NO_2$, -CN, $-NH_2$, -NHA, $-N(A)_2$, $-N^+H_3$, $-N^+H_2A$, $-N^+H(A_2)$, $-N^+(A)_3$, -NHCOA, -N(A)COA, -CHO, -C(A)=O, $-CH(OA)_2$, $-C(A)(OA)_2$, $-C(OA)_3$, -CH=N-A, -C(A)=N-A, -N=CH-A, $-N=C(A)_2$, -N=N-A, $-COO^-$, -COOH, -COOA, $-CONH_2$, -CONHA, $-CON(A)_2$, $-NHCONH_2$, -NHCONHA, $-NHCON(A)_2$, $-N(A)CONH_2$, -N(A)CONHA, $-N(A)CON(A)_2$, $-SO_2A$, $-SO_3^-$, $-SO_3H$, $-SO_3A$, $-PO_3^-$, $-PO(OA)_2$, $-Si(A)_3$, $-OSi(A)_3$, $-Si(OA)_2(A)$ or $-Si(OA)_3$, each A being independently of the others alkyl, alkenyl,

alkynyl, cycloalkyl, cycloalkenyl, aralkyl, aryl or heteroaryl, each of which can be uninterrupted or interrupted by one or more hetero atoms, such as N, O, P and S, for example in the form of a polyalkylene glycol chain, pyrrolidinyl, piperidyl, piperazinyl, morpholinyl, oxybisphenylene or heteroaryl, such as pyridyl, furyl, thienyl or phenothiazinyl.

A is typically C_1-C_{24}alkyl, C_2-C_{24}alkenyl, C_2-C_{24}alkynyl, C_3-C_{24}cycloalkyl, C_3-C_{24}cycloalkenyl, C_7-C_{24}aralkyl, C_6-C_{24}aryl or C_4-C_{12}heteroaryl.

It will be understood that different As can also be combined, such as, for example, in chromanyl, phosphindolinyl or 1-phenyl-2-pyrazolinyl, that is to say, for example, in substituted form azo-3-methyl-5-oxo-1-phenyl-2-pyrazolin-(4)-yl. It is also possible for alkylene, arylene or aralkylene to be used in place of two As, for example morpholino in place of methyl-3-oxabutyl-amino or 4-methyl-piperidino in place of ethyl-3-azabutyl-amino.

When G_1 contains a radical A, that radical can be unsubstituted or substituted by from 1 to 5 identical or different substituents G_2, each G_2 being as defined for G_1, except that G_2 can only be unsubstituted or mono-substituted by G_3, where G_3 likewise is as defined for G_1, except that G_3 is not further substituted.

Especially the following substituents may be mentioned as G_1: $\cdot CH_2\cdot CH_2\cdot OH$, $\cdot CH_2\cdot O\cdot CH_3$, $\cdot CH_2\cdot O\cdot (CH_2)_7\cdot CH_3$, $\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_3$, $\cdot CH_2\cdot CH(OCH_3)_2$, $\cdot CH_2\cdot CH_2\cdot CH(OCH_3)_2$, $\cdot CH_2\cdot C(OCH_3)_2\cdot CH_3$, $\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot CH_3$, $\cdot (CH_2)_3\cdot OH$, $\cdot (CH_2)_6\cdot OH$, $\cdot (CH_2)_7\cdot OH$, $\cdot (CH_2)_8\cdot OH$, $\cdot (CH_2)_9\cdot OH$, $\cdot (CH_2)_{10}\cdot OH$, $\cdot (CH_2)_{11}\cdot OH$, $\cdot (CH_2)_{12}\cdot OH$, $\cdot CH_2\cdot Si(CH_3)_3$, $\cdot CH_2\cdot CH_2\cdot O\cdot Si(CH_3)_2\cdot C(CH_3)_3$, $\cdot (CH_2)_3\cdot O\cdot Si(CH_3)_2\cdot C(CH_3)_3$, $\cdot (CH_2)_4\cdot O\cdot Si(C_6H_5)_2\cdot C(CH_3)_3$, $\cdot (CH_2)_5\cdot O\cdot Si(CH(CH_3)_2)_3$, $\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot C(CH_3)_2\cdot OH$, $\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot OH$, $\cdot CH_2\cdot C(CH_3)_2\cdot CH_2\cdot OH$, $\cdot CH_2\cdot C(CH_2\cdot OH)_3$, $\cdot CH_2\cdot CH(OH)\cdot CH_3$, $\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, $-CH_2CH_2O-$  , $-(CH_2)_3O-$,

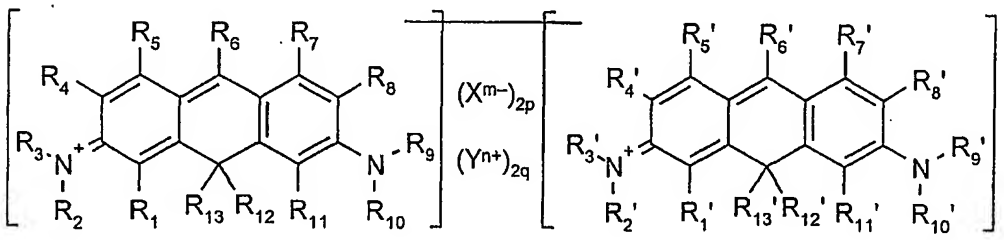
$-CH_2CH_2-$, $-CH_2CH_2-$, $-CH_2-$, $-CH_2CH_2-$,

$-CH_2-$, $-CH_2-$, $-(CH_2)_5-$, $-(CH_2)_3O-$, $-(CH_2)_2O-$

and $-(CH_2)_2CH{=}N{-}R_{14}$, wherein R_{14} is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, C_2-C_{24}alkynyl,

C_3-C_{24}cycloalkyl, C_3-C_{24}cycloalkenyl, C_7-C_{24}aralkyl, C_6-C_{24}aryl, C_4-C_{12}heteroaryl or C_1-C_{12}heterocycloalkyl, each unsubstituted or substituted by one or more identical or different substituents G_2, or is a metal complex. When R_{14} is C_1-C_{24}alkyl, it may be uninterrupted or interrupted by from 1 to 3 oxygen and/or silicon atoms. G_2 or G_3 may especially advantageously be alkyl unsubstituted or substituted by one or two hydroxy substituents or by a metallocenyl or azo metal complex radical. Such radicals G_1 are of very special importance as R_6.

The compound of formula (I) may optionally also be a dimer of formula



(II)

wherein R_1' to R_{13}' have the same meanings as R_1 to R_{13} and an R substituent selected from R_1 to R_{13} is bonded to an R' substituent selected from R_1' to R_{13}', for example *via* a direct bond, an alkylene group or a hetero atom, or an R' substituent selected from R_1' to R_{13}' is a direct bond to an R substituent selected from R_1 to R_{13}.

Great importance is attached especially to compounds of formula (II) wherein R_6 is bonded to R_6', or R_6' is a direct bond to R_6.

When the numbers p and q are not whole numbers, it is to be understood by formulae (I) and (II) that there is a mixture of a certain molar composition, the individual components of which may also have different stoichiometry.

Alkyl, alkenyl or alkynyl may be straight-chain or branched. Alkenyl is alkyl that is mono- or poly-unsaturated, wherein two or more double bonds may be isolated or conjugated. Alkynyl is alkyl or alkenyl that is double-unsaturated one or more times, wherein the triple bonds may be isolated or conjugated with one another or with double bonds. Cycloalkyl or cycloalkenyl is monocyclic or polycyclic alkyl or alkenyl, respectively.

C_1-C_{24}Alkyl can therefore be, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-methyl-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, n-hexyl, heptyl, n-octyl, 1,1,3,3-tetramethylbutyl, 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl or tetracosyl.

C_3-C_{24}Cycloalkyl can therefore be, for example, cyclopropyl, cyclopropyl-methyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexyl-methyl, trimethyl-cyclohexyl, thujyl, norbornyl, bornyl, norcaryl, caryl, menthyl, norpinyl, pinyl, 1-adamantyl, 2-adamantyl, 5α-gonyl or 5ξ-pregnyl.

C_2-C_{24}Alkenyl is, for example, vinyl, allyl, 2-propen-2-yl, 2-buten-1-yl; 3-buten-1-yl, 1,3-butadien-2-yl, 2-penten-1-yl, 3-penten-2-yl, 2-methyl-1-buten-3-yl, 2-methyl-3-buten-2-yl, 3-methyl-2-buten-1-yl, 1,4-pentadien-3-yl, or any desired isomer of hexenyl, octenyl, nonenyl, decenyl, dodecenyl, tetradecenyl, hexadecenyl, octadecenyl, eicosenyl, heneicosenyl, docosenyl, tetracosenyl, hexadienyl, octadienyl, nonadienyl, decadienyl, dodecadienyl, tetradecadienyl, hexadecadienyl, octadecadienyl or eicosadienyl.

C_3-C_{24}Cycloalkenyl is, for example, 2-cyclobuten-1-yl, 2-cyclopenten-1-yl, 2-cyclohexen-1-yl, 3-cyclohexen-1-yl, 2,4-cyclohexadien-1-yl, 1-*p*-menthen-8-yl, 4(10)-thujen-10-yl, 2-norbornen-1-yl, 2,5-norbornadien-1-yl, 7,7-dimethyl-2,4-norcaradien-3-yl or camphenyl.

C_1-C_{24}Alkoxy is O—C_1-C_{24}alkyl, and C_1-C_{24}alkylthio is S—C_1-C_{24}alkyl.

C_2-C_{24}Alkynyl is, for example, 1-propyn-3-yl, 1-butyn-4-yl, 1-pentyn-5-yl, 2-methyl-3-butyn-2-yl, 1,4-pentadiyn-3-yl, 1,3-pentadiyn-5-yl, 1-hexyn-6-yl, cis-3-methyl-2-penten-4-yn-1-yl, trans-3-methyl-2-penten-4-yn-1-yl, 1,3-hexadiyn-5-yl, 1-octyn-8-yl, 1-nonyn-9-yl, 1-decyn-10-yl or 1-tetracosyn-24-yl.

C_7-C_{24}Aralkyl is, for example, benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, 9-fluorenyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω-phenyl-octyl, ω-phenyl-dodecyl or 3-methyl-5-(1',1',3',3'-tetramethyl-butyl)-benzyl. C_7-C_{24}Aralkyl can also be, for example, 2,4,6-tri-tert-butyl-benzyl or 1-(3,5-dibenzyl-phenyl)-3-methyl-2-propyl. When C_7-C_{24}aralkyl is substituted, either the alkyl moiety or

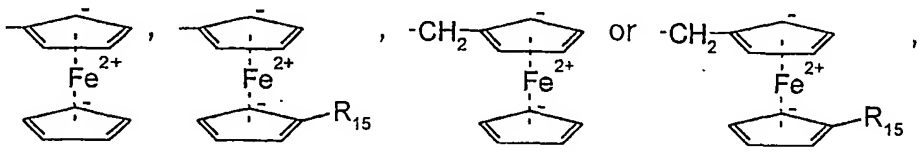
the aryl moiety of the aralkyl group can be substituted, the latter alternative being preferred.

C_6-C_{24}Aryl is, for example, phenyl, naphthyl, biphenylyl, 2-fluorenyl, phenanthryl, anthracenyl or terphenylyl.

Halogen is chlorine, bromine, fluorine or iodine, preferably chlorine or bromine.

C_4-C_{12}Heteroaryl is an unsaturated or aromatic radical having 4n+2 conjugated π-electrons, for example 2-thienyl, 2-furyl, 1-pyrazolyl, 2-pyridyl, 2-thiazolyl, 2-oxazolyl, 2-imidazolyl, isothiazolyl, triazolyl or any other ring system consisting of thiophene, furan, pyridine, thiazole, oxazole, imidazole, isothiazole, thiadiazole, triazole, pyridine and benzene rings and unsubstituted or substituted by from 1 to 6 ethyl, methyl, ethylene and/or methylene substituents.

Furthermore, aryl and aralkyl can also be aromatic groups bonded to a metal, for example in the form of metallocenes of transition metals known *per se*, more especially



wherein R_{15} is CH_2OH, CH_2OA, COOH, COOA or COO^-.

C_1-C_{12}Heterocycloalkyl is an unsaturated or partially unsaturated ring system radical, for example tetrazolyl, pyrrolidyl, piperidyl, piperazinyl, imidazolinyl, pyrazolidinyl, pyrazolinyl, morpholinyl, quinuclidinyl or another C_4-C_{12}heteroaryl that is mono- or poly-hydrogenated.

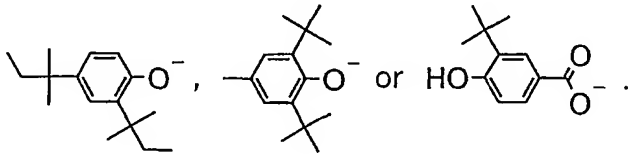
Y^{n+} as a metal, ammonium or phosphonium cation is, for example, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Sn^{2+}, Cr^{3+}, La^{3+}, methylammonium, ethylammonium, pentadecylammonium, isopropylammonium, dicyclohexylammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, benzyltrimethylammonium, benzyltriethylammonium, methyltrioctylammonium, tridodecylmethylammonium, tetrabutylphosphonium, tetraphenylphosphonium, butyltriphenylphosphonium or ethyl-

triphenylphosphonium, or protonated Primen 81R™ or Rosin Amin D™.

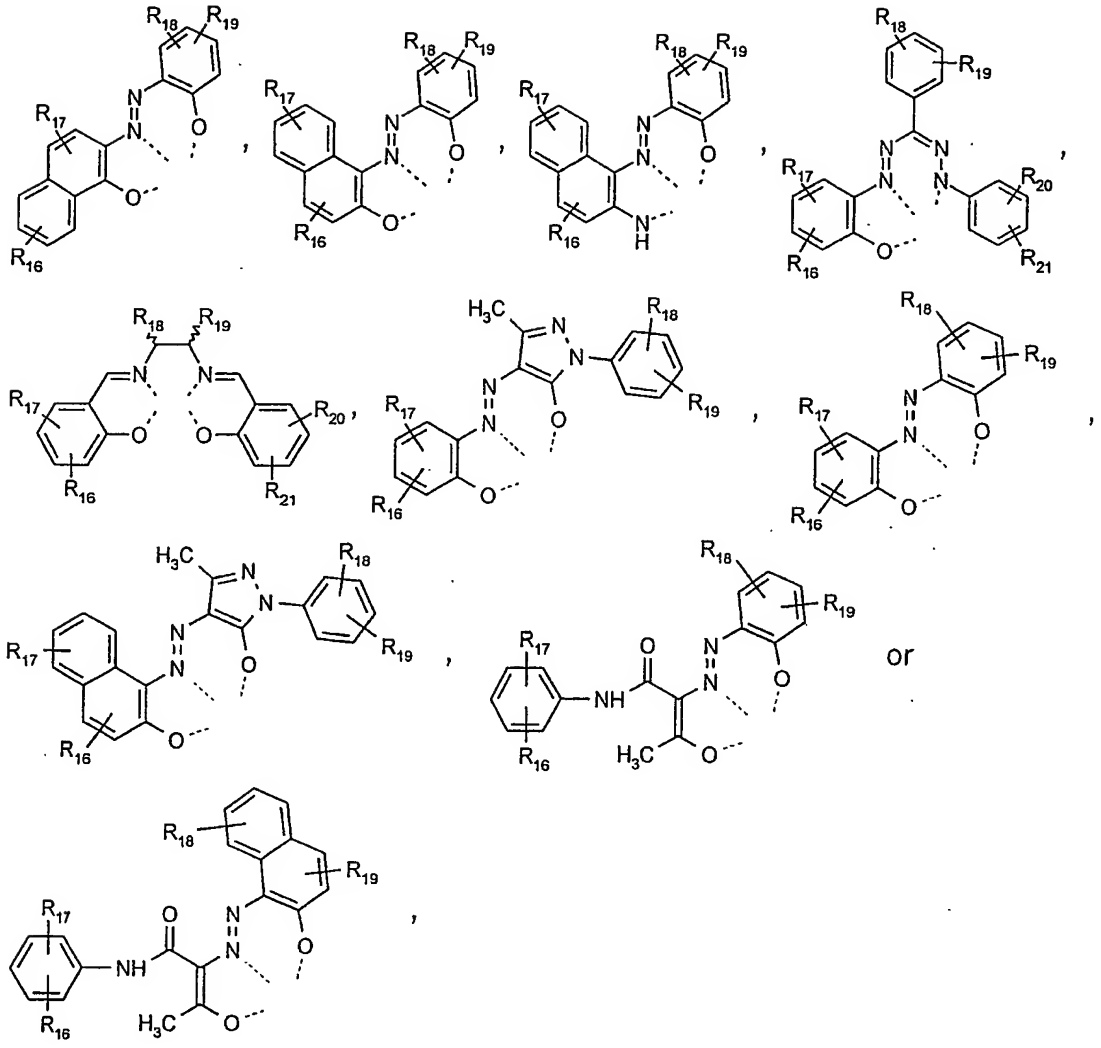
X^{m-} as an inorganic, organic or organometallic anion is, for example, the anion of a mineral acid, the conjugate base of an organic acid or an organometal complex anion, for example fluoride, chloride, bromide, iodide, perchlorate, periodate, nitrate, ½ carbonate, hydrogen carbonate, C_1-C_4alkyl sulfate, ½ sulfate, hydrogen sulfate, ⅓ phosphate, ½ hydrogen phosphate, dihydrogen phosphate, ½ C_1-C_4alkanephosphonate, C_1-C_4alkane-C_1-C_{12}alkyl-phosphonate, di-C_1-C_4alkylphosphinate, tetrafluoroborate, hexafluorophosphate, hexafluoro-antimonate, acetate, trifluoroacetate, heptafluorobutyrate, ½ oxalate, methane-sulfonate, trifluoromethanesulfonate, tosylate, benzenesulfonate, p-chloro-benzenesulfonate, p-nitrobenzenesulfonate, an alcoholate, phenolate (e.g. phenolate itself), carboxylate (also e.g. benzoate), sulfonate or phosphonate) or a negatively charged metal complex.

The person skilled in the art will readily recognise that it is also possible to use other anions with which he is familiar. It will be self-evident to him that $\frac{1}{x}$ of an inorganic, organic or organometallic anion having x negative charges, for example $½ \cdot SO_4^{2-}$, is a multiply charged anion which neutralises several singly charged cations or a cation having x charges, as the case may be.

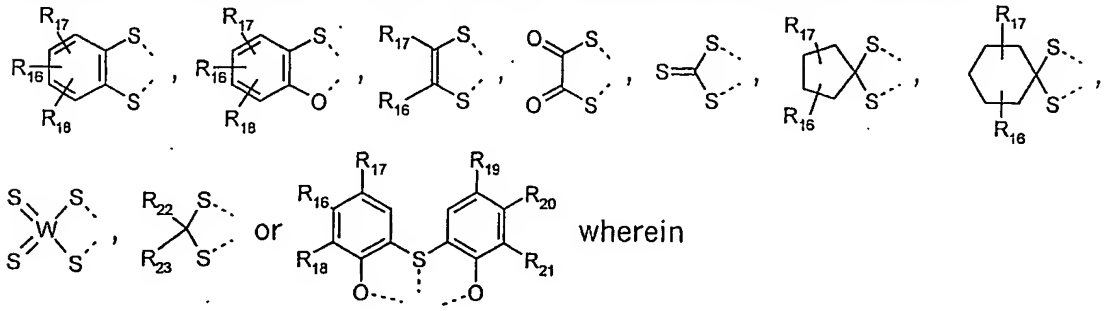
Phenolates or carboxylates are, for example, anions of C_1-C_{12}alkylated, especially tert-C_4-C_8alkylated, phenols or benzoic acids, such as



When X^{m-} is an organometallic anion, it is preferably a metal complex of formula $[(L_1)M_1(L_2)]^{m-}$ (III) or $[(L_3)M_2(L_4)]^-$ (IV), wherein M_1 and M_2 are a transition metal, preferably M_1 being Cr^{3+} or Co^{3+} and M_2 being Ni^{2+}, Co^{2+} or Cu^{2+}, m is a number from 1 to 6, L_1 and L_2 are each independently of the other a ligand of formula



and L_3 and L_4 are each independently of the other a ligand of formula



wherein

R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21} are each independently of the others hydrogen, halogen, cyano, R_{24}, NO_2, $NR_{24}R_{25}$, $NHCO{\cdot}R_{24}$, $NHCOOR_{24}$, $SO_2{-}R_{24}$, SO_2NH_2,

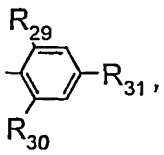
SO_2NHR_{24}, $SO_2NR_{24}R_{25}$, SO_3^- or SO_3H, preferably hydrogen, chlorine, SO_2NH_2 or SO_2NHR_{24}, and R_{22} and R_{23} are each independently of the other CN, $CONH_2$, $CONHR_{24}$, $CONR_{24}R_{25}$, $COOR_{24}$ or COR_{24}, wherein R_{24} and R_{25} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}alkoxy-C_2-C_{12}alkyl, C_7-C_{12}aralkyl or C_6-C_{12}aryl, preferably C_1-C_4alkyl, each unsubstituted or substituted by hydroxy, halogen, sulfato, C_1-C_6alkoxy, C_1-C_6alkylthio, C_1-C_6alkylamino or by di-C_1-C_6alkylamino, or R_{24} and R_{25} together are C_4-C_{10}heterocycloalkyl; it also being possible for R_{16} and R_{17}, R_{18} and R_{19}, and/or R_{20} and R_{21} to be bonded together in pairs in such a manner that a 5- or 6-membered ring is formed.

Reference is made by way of illustration, but on no account as a limitation, to the individual compounds disclosed in US-5 219 707, US-6 168 843, US-6 242 067, WO-01/19923, WO-01/62853, EP-A-1 125 987, EP-A-1 132 902, JP-A-06/199045, JP-A-07/262604, JP-A-2000/190642 and JP-A-2000/198273.

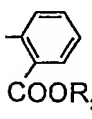
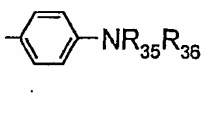
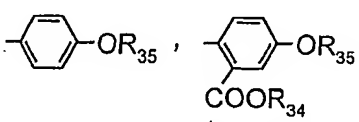
It is also possible, however, to use any other known transition metal complex anion that contains, for example, a phenolic or phenylcarboxylic azo compound as ligand L_1 or L_2.

Preference is given to compounds of formula (I) wherein R_1, R_4, R_5, R_7, R_8 and R_{11} are hydrogen; R_2, R_3, R_9, R_{10}, R_{12} and R_{13} are each independently of the others methyl, ethyl or R_{14}, it being possible for R_2 and R_3, R_9 and R_{10}, R_{12} and R_{13} and/or R_9 and R_{10} also to be bonded together in pairs *via* a direct bond, methylene, -O- or -N(C_1-C_4alkyl); and R_6 is hydrogen or C_1-C_{12}alkyl, C_6-C_{12}aryl or C_7-C_{13}aralkyl, each unsubstituted or mono- to tetra-substituted by halogen, $-O^-$, $-OR_{26}$, -CN, $-NR_{26}R_{27}$, $-N^+R_{26}R_{27}R_{28}$, $-N(R_{26})COR_{27}$, $-COO^-$, $-COOR_{26}$, $-CONR_{26}R_{27}$, R_{14} or by $-N(R_{26})COR_{27}R_{28}$, wherein R_{26}, R_{27} and R_{28} are each independently of the others C_1-C_{12}alkyl, C_6-C_{12}aryl or C_7-C_{13}aralkyl;

all the bridging possibilities, limitations and definitions indicated above otherwise remaining unchanged.

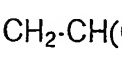
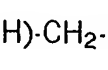
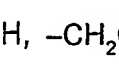
When R_6 is unsubstituted or substituted C_6-C_{12}aryl, it is preferably  ,

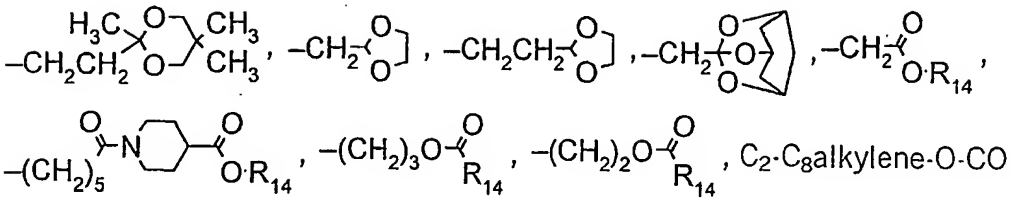
wherein R_{29}, R_{30} and R_{31} are each independently of the others hydrogen, halogen, $COOR_{32}$, OR_{32} or $NR_{32}R_{33}$, wherein R_{32} and R_{33} are each independently of the other hydrogen or C_1-C_{12}alkyl, C_2-C_{12}alkenyl, C_1-C_{12}cycloalkyl, C_2-C_{12}cycloalkenyl, C_6-C_{12}aryl or C_7-C_{13}aralkyl, each unsubstituted or substituted by one or two hydroxy substituents or by a metallocenyl or azo metal complex radical and uninterrupted or interrupted by 1, 2, 3, 4 or 5 oxygen and/or silicon atoms. R_{29} is preferably hydrogen, carboxy or COO-C_1-C_8alkyl, R_{30} is hydrogen or halogen, and R_{31} is hydrogen, C_1-C_8alkoxy or di-C_1-C_8alkylamino.

Special preference is given to compounds of formula (I) wherein R_6 is  ,  ,  ,  ,  , or R_{37}, and

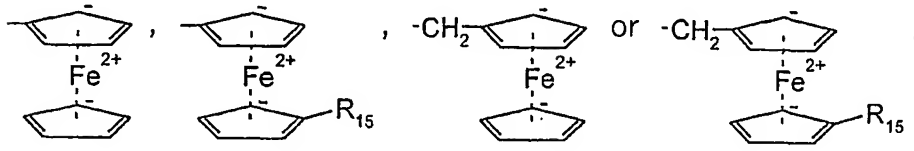
R_{34}, R_{35} and R_{36} are each independently of the others hydrogen or R_{37}.

When R_6 is substituted by R_{37}, then it is preferably substituted by a single R_{37}. The total number of radicals R_{37} in formula (I) is preferably 0, 1 or 2, especially 0 or 1. The total number of radicals R_{37} in formula (II) is preferably 0, 1, 2, 3 or 4, especially 0 or 2.

R_{37} is preferably alkyl uninterrupted or interrupted by from 1 to 3 oxygen and/or silicon atoms and unsubstituted or substituted by one or two hydroxy substituents or by a metallocenyl or azo metal complex radical, especially C_1-C_8alkyl, CH_2-CH_2-OH, -CH_2-O-CH_3, -CH_2-O-$(CH_2)_7$-CH_3, -CH_2-CH_2-O-CH_2-CH_3, -CH_2-$CH(OCH_3)_2$, -CH_2-CH_2-$CH(OCH_3)_2$, -CH_2-$C(OCH_3)_2$-CH_3, -CH_2-CH_2-O-CH_2-CH_2-O-CH_3, -$(CH_2)_3$-OH, -$(CH_2)_6$-OH, -$(CH_2)_7$-OH, -$(CH_2)_8$-OH, -$(CH_2)_9$-OH, -$(CH_2)_{10}$-OH, -$(CH_2)_{11}$-OH, -$(CH_2)_{12}$-OH, -CH_2-$Si(CH_3)_3$, -CH_2-CH_2-O-$Si(CH_3)_2$-$C(CH_3)_3$, -$(CH_2)_3$-O-$Si(CH_3)_2$-$C(CH_3)_3$, -$(CH_2)_4$-O-$Si(C_6H_5)_2$-$C(CH_3)_3$, -$(CH_2)_5$-O-$Si(CH(CH_3)_2)_3$, -CH_2-CH_2-$CH(CH_3)$-CH_2-CH_2-$CH(OH)$-$C(CH_3)_2$-OH, -CH_2-$CH(CH_3)$-CH_2-OH, -CH_2-$C(CH_3)_2$-CH_2-OH, -CH_2-$C(CH_2$-OH$)_3$, -CH_2-$CH(OH)$-CH_3, -CH_2-$CH(OH)$-CH_2-OH,  ,  ,  ,

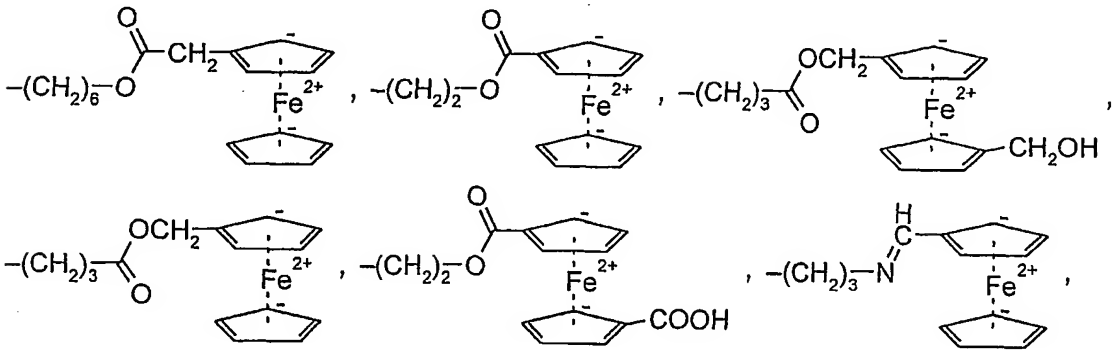


C_2-C_8alkylene-COO-Đ or C_2-C_8alkylene-N=CH-Đ, wherein Đ is

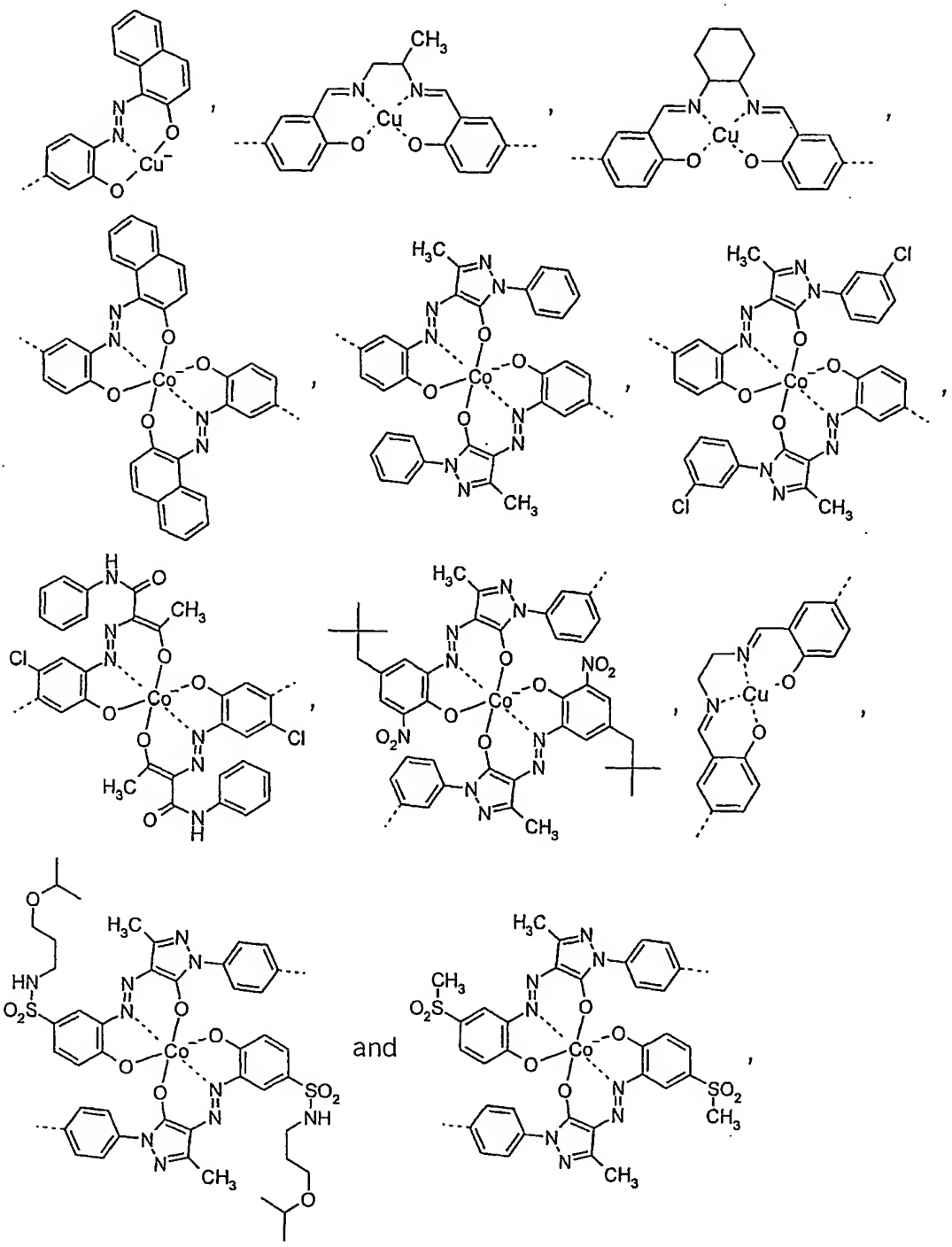


Azo metal complex radicals have, for example, the formula -$[(L_1)M_1(L_2)]^{m-}$.

Metallocenyl radicals preferably contain as metal Ni, Co, Cu, Ti or especially Fe. For example, R_{37} in formula (I) or (II) as a metallocenyl radical may be



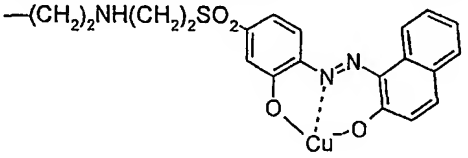
[-C_2-C_8alkylene-SO_2]$_2$-Ø-Š, [-C_2-C_8alkylene-O-C_2-C_8alkylene-$NHSO_2$]$_2$-Ø-Š, [-C_2-C_8alkylene-$NHSO_2$]$_2$-Ø-Š, [-C_2-C_8alkylene-NH-C_2-C_8alkylene-SO_2]$_2$-Ø-Š or [-C_2-C_8alkylene-N(C_1-C_8alkyl)-C_2-C_8alkylene-SO_2]$_2$-Ø-Š; or in formula (II) as an azo metal complex radical may be [-C_2-C_8alkylene-SO_2]$_2$-Ø-, [-C_2-C_8alkylene-$NHSO_2$]$_2$-Ø-, [-C_2-C_8alkylene-O-C_2-C_8alkylene-$NHSO_2$]$_2$-Ø-, [-C_2-C_8alkylene-NH-C_2-C_8alkylene-SO_2]$_2$-Ø- or [-C_2-C_8alkylene-N(C_1-C_8alkyl)-C_2-C_8alkylene-SO_2]$_2$-Ø-, wherein Š is SO_3^-, SO_2-C_1-C_8alkyl, $SO_2NR_{39}R_{40}$, R_{39} and R_{40} are each independently of the other hydrogen or C_1-C_{12}alkyl, C_2-C_{12}alkenyl, C_1-C_{12}cycloalkyl, C_2-C_{12}cycloalkenyl, C_6-C_{12}aryl or C_7-C_{13}aralkyl, each uninterrupted or interrupted by from 1 to 5 oxygen and/or silicon atoms and unsubstituted or substituted by one or two hydroxy substituents, and Ø is the bivalent radical of an organometallic anion selected from the group consisting of

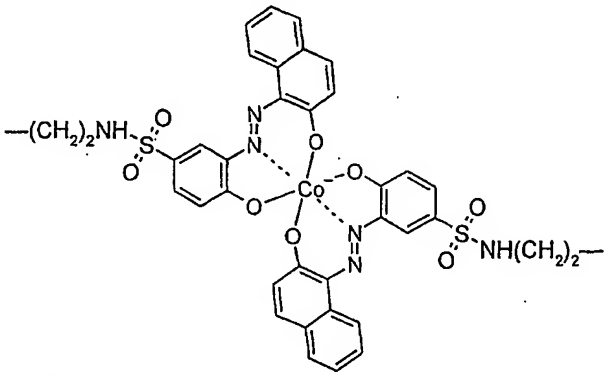


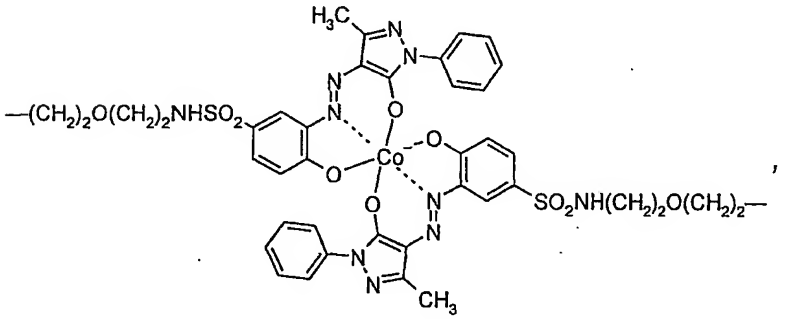
and those of the formulae Q1, Q2, Q3, Q4, Q5, Q6, Q7, Q8, Q9, Q10, Q11, Q12, Q13, Q14, Q15, Q16, Q17, Q18, Q19, Q20, Q21, Q22, Q23, Q24 and Q25 given hereinbelow.

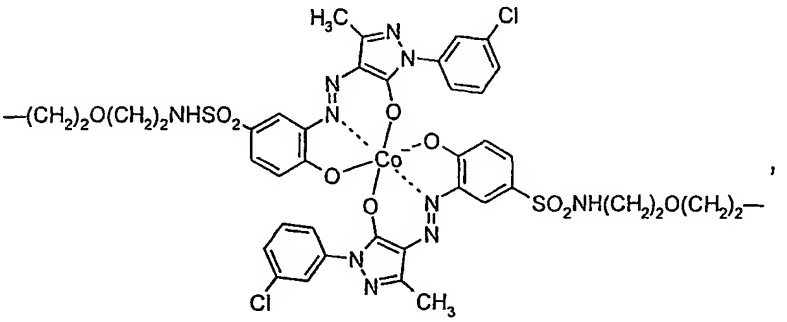
-Alkylene-SO_2-Ø, -alkylene-$NHSO_2$-Ø, -alkylene-O-alkylene-$NHSO_2$-Ø,

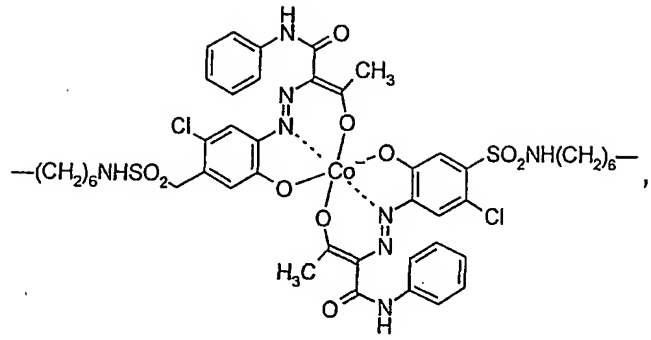
-alkylene-NH-alkylene-SO_2-Ø or -alkylene-N(alkyl)-alkylene-SO_2-Ø are preferably -$(CH_2)_2$-SO_2-Ø, -$(CH_2)_2$-$NHSO_2$-Ø, -$(CH_2)_2$-O-$(CH_2)_2$-$NHSO_2$-Ø, -$(CH_2)_2$-NH-$(CH_2)_2$-SO_2-Ø, -$(CH_2)_6$-$NHSO_2$-Ø or -$(CH_2)_2$-$N(C_4H_9)$-$(CH_2)_2$-SO_2-Ø.

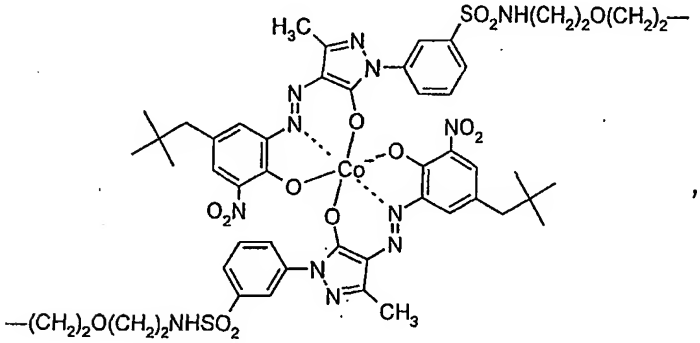
Of special interest are compounds of formula (I) substituted by azo metal complex radicals such as, for example,  , and

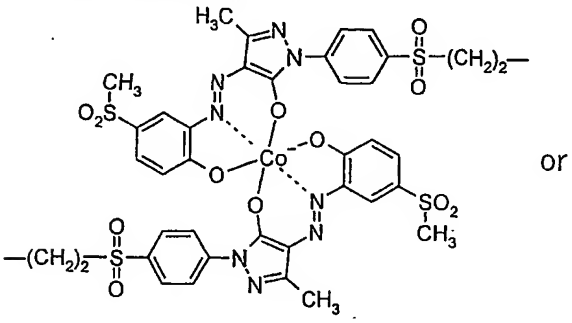
also compounds of formula (II) wherein two radicals of formula (I) are linked *via* a bridge of formula  ,

 ,

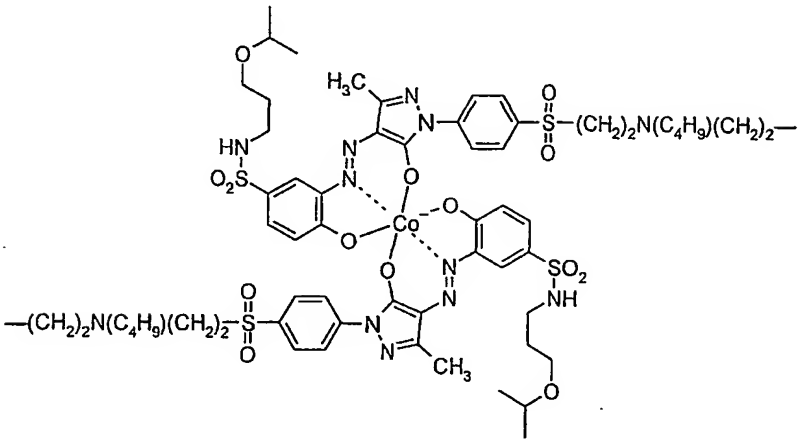
 ,







or



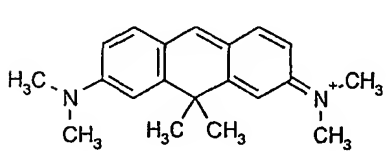
Those preferences apply to each of the sub-structures contained in formula (I) or (II), in each case independently of any other sub-structures which may be present, provided that the condition inherent in formula (I) or (II) is fulfilled,

i.e. that the resulting compound does not have an excess positive or negative charge. Sub-structures of formula (I) or (II) are to be understood as including their three components carbopyronine, $(X^{m-})_p$ and $(Y^{n+})_q$ that are not bonded to one another.

Special preference is given also to compounds of formula (I) or (II) wherein Y^{n+} is $[NH_2R_{38}R_{39}]^+$, R_{38} being hydrogen or C_1-C_{12}alkyl and R_{39} being C_1-C_{24}alkyl or C_7-C_{24}aralkyl, and R_{38} and R_{39} together having from 8 to 25 carbon atoms.

Special preference is given also to compounds of formula (I) or (II) wherein m and n are each the number 1, p is a number from 1 to 2½, and q is a number from 0 to 1½, the sum of positive charges in formula (I) or (II) being equal to the sum of negative charges.

Very special preference is given to the compounds of formula $[G^+]_1 \cdot [Q^-]_1$ (V) or $[G^+]_1(F)_r(Cl)_s \cdot [Q^-]_1$ (VI), wherein G^+ is a cation selected from the group consisting of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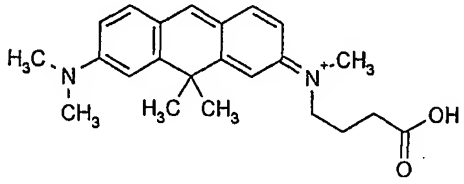
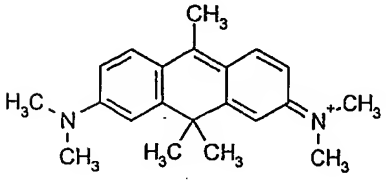

(G2),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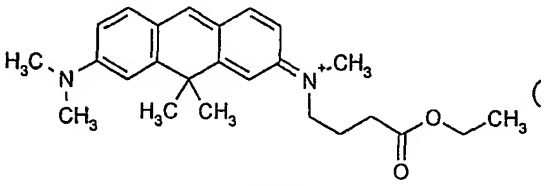
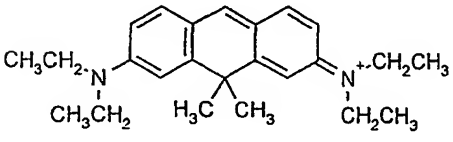

(G4),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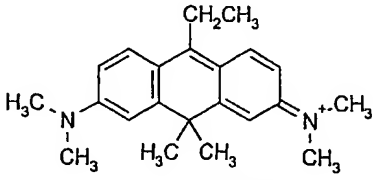
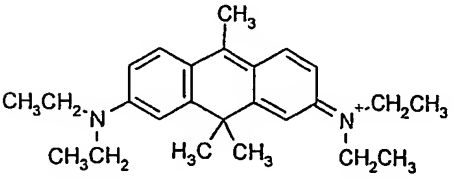
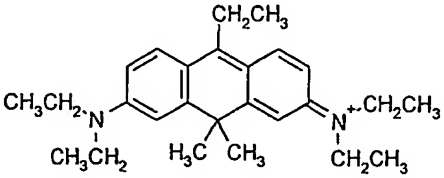
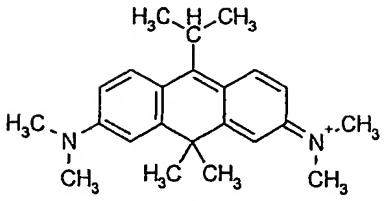
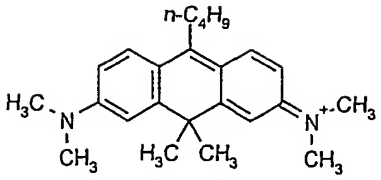

(G6),


(G7),

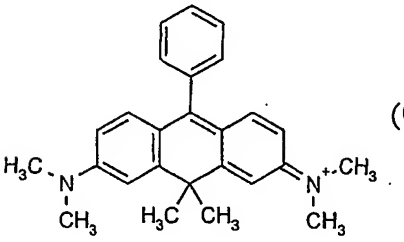

(G8),



(G9),



(G10),



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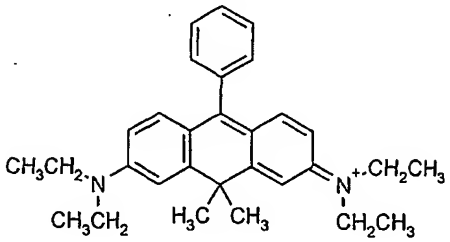

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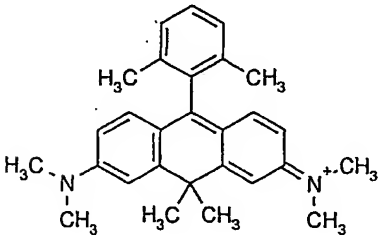

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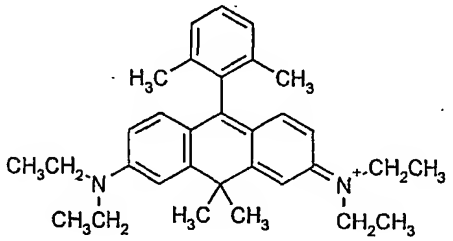

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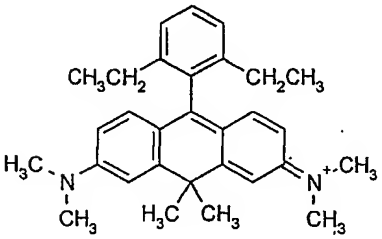

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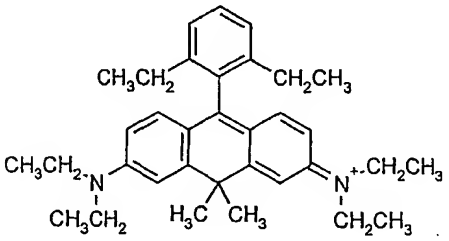

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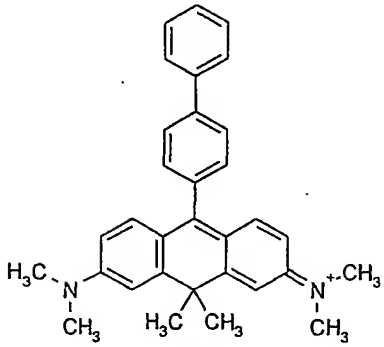

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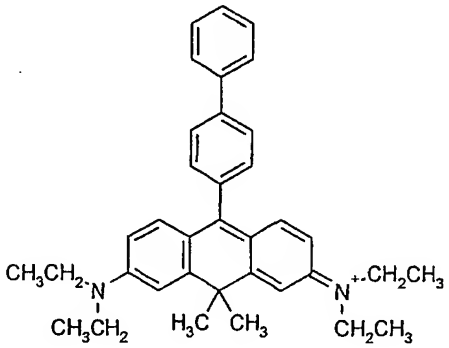

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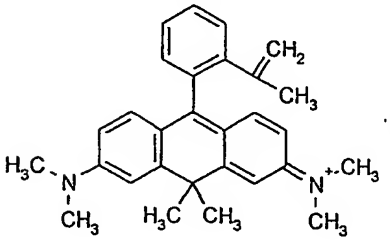

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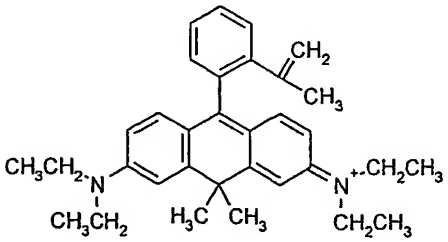

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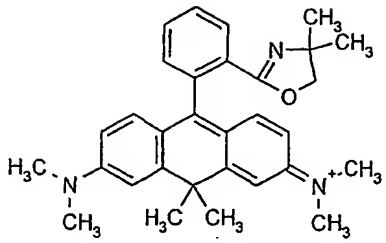
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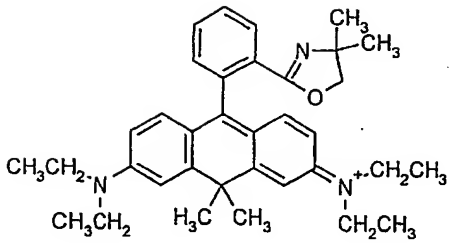
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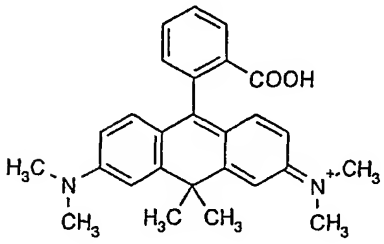
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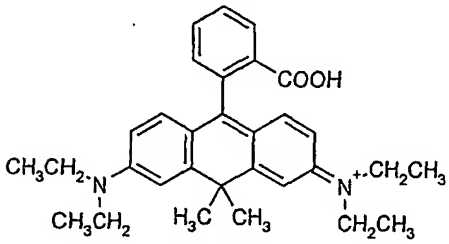
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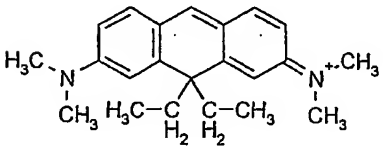
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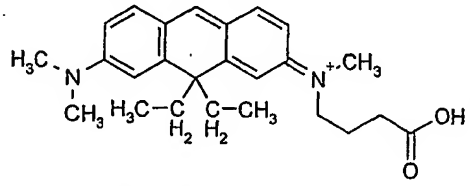
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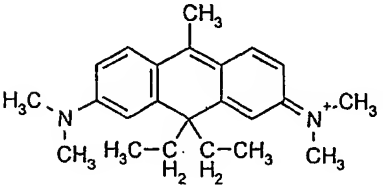
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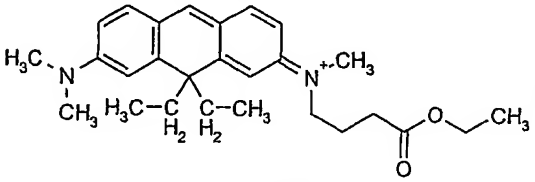
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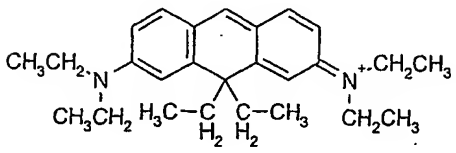
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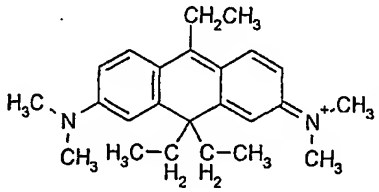
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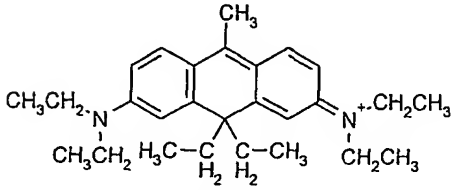
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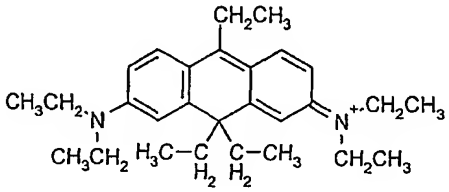
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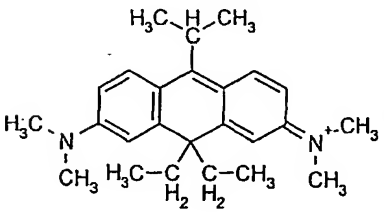
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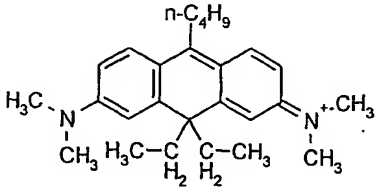
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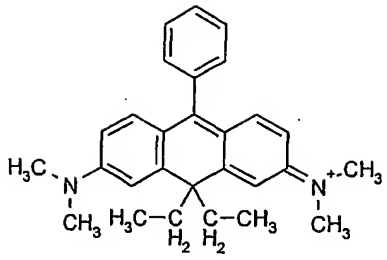

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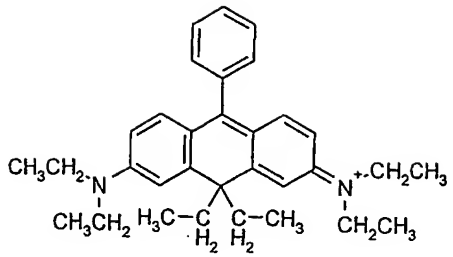

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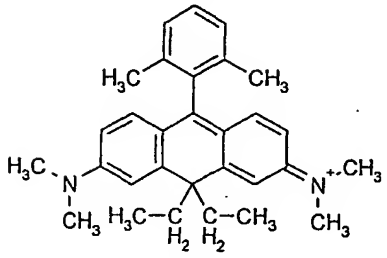

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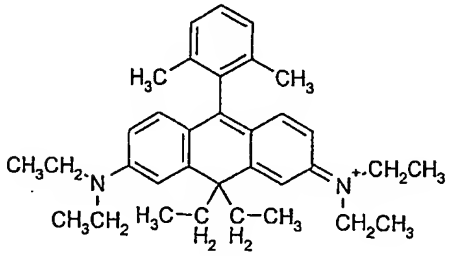

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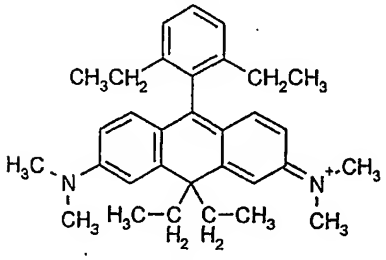

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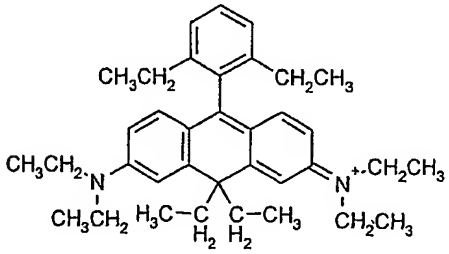

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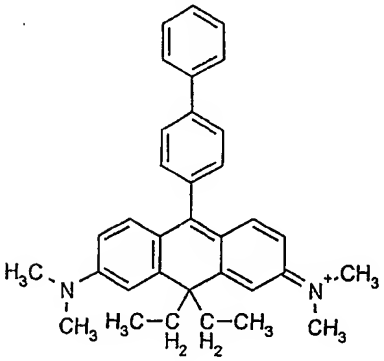

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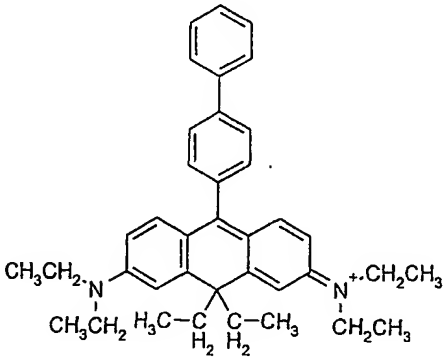

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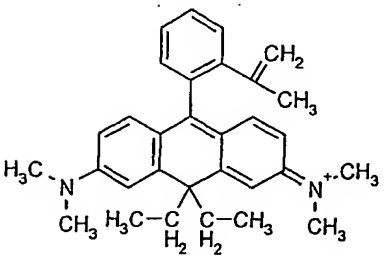

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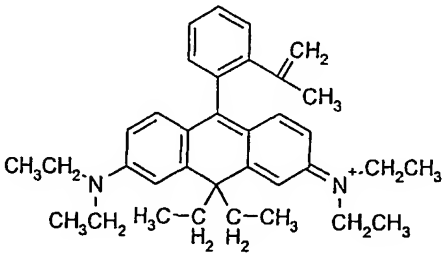

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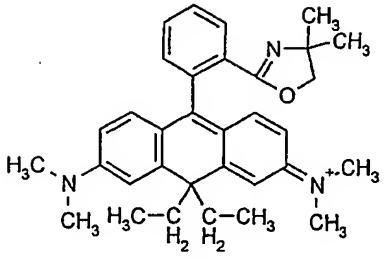
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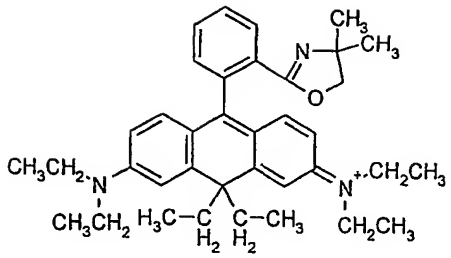
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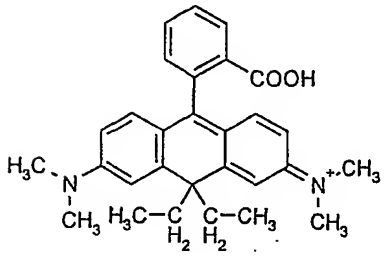
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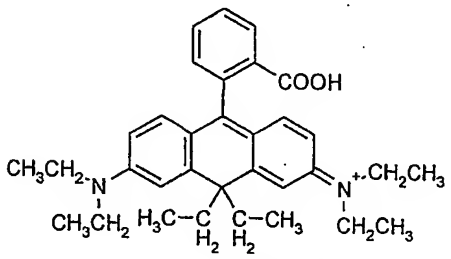
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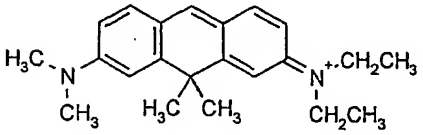
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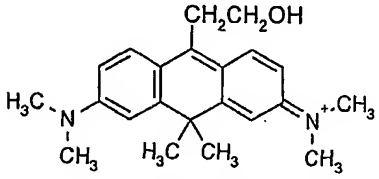
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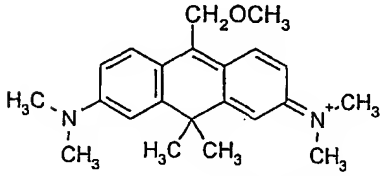
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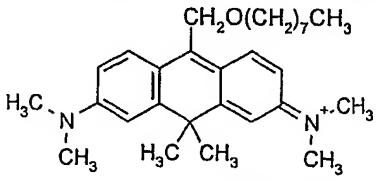
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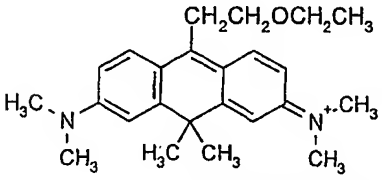
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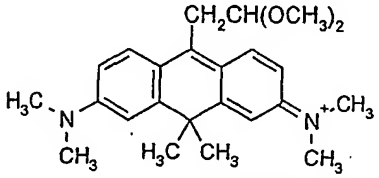
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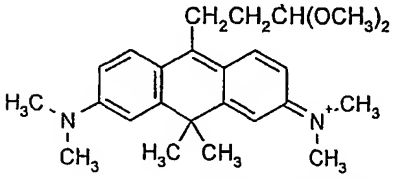
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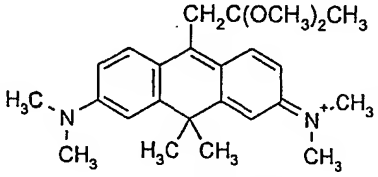
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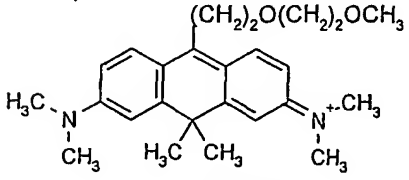
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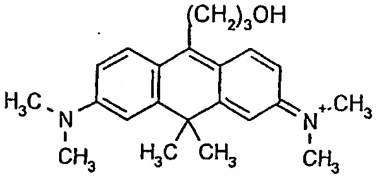
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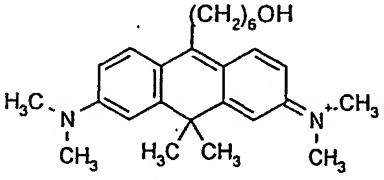
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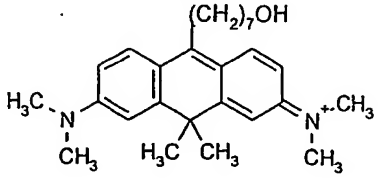
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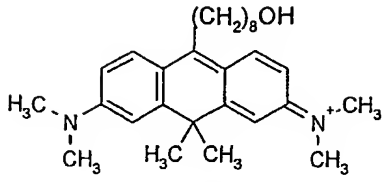
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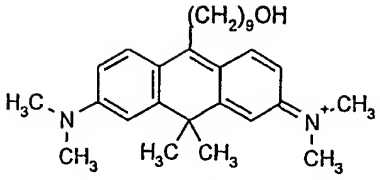
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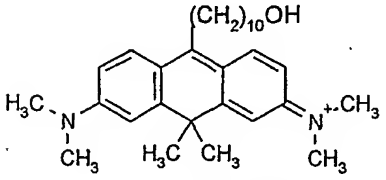
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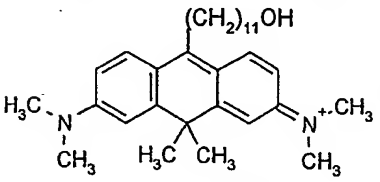
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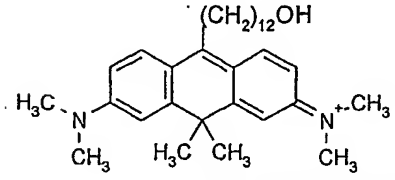
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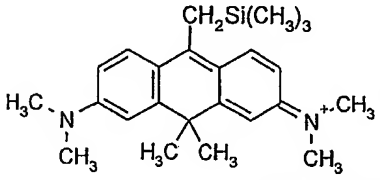
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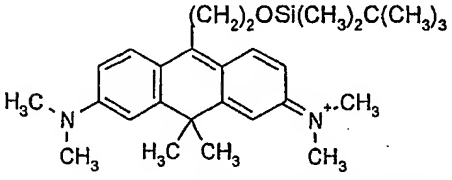
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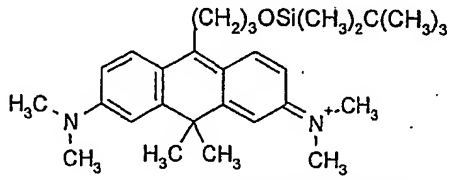
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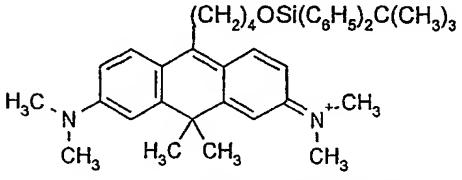
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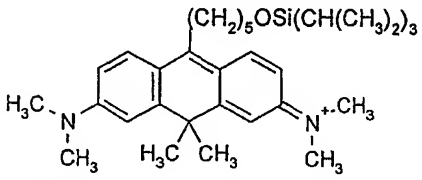
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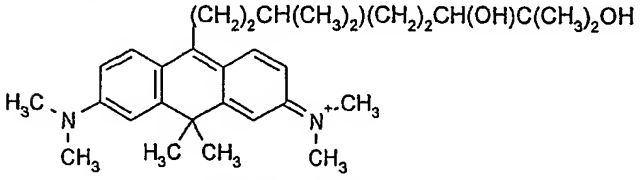
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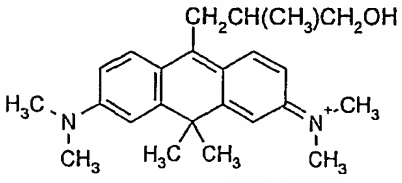
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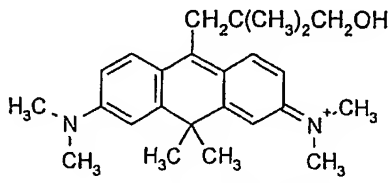
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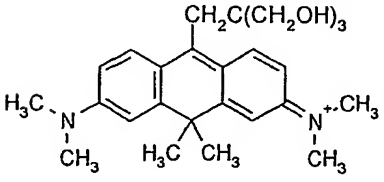
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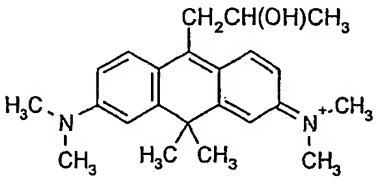
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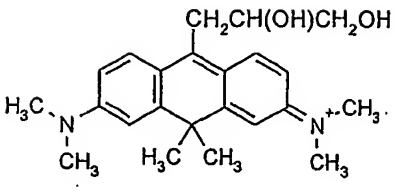
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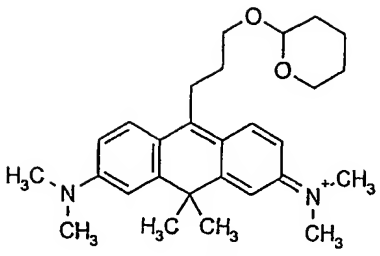
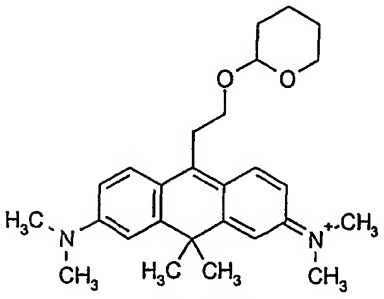
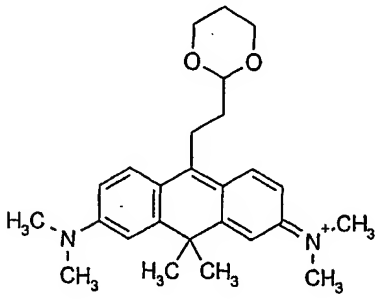
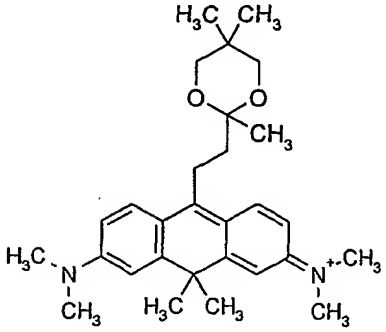
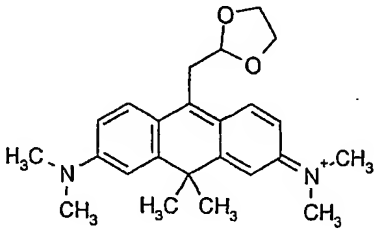
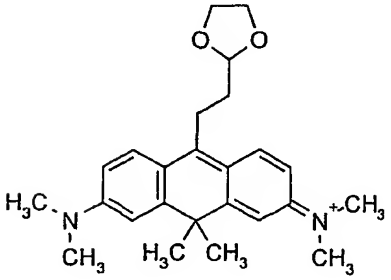

(G77),

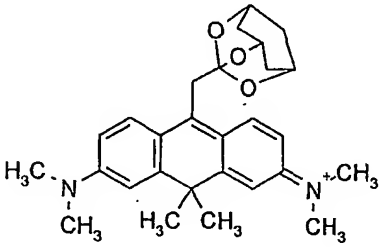

(G78),


(G79),

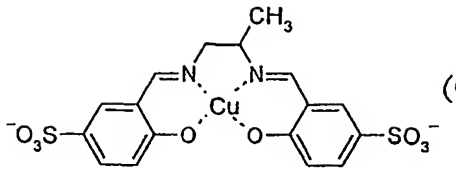

(G80),


(G81),

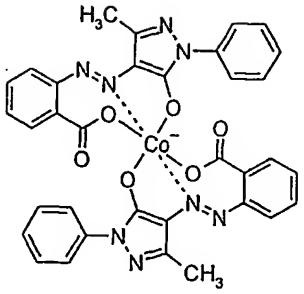

(G82),


(G83),

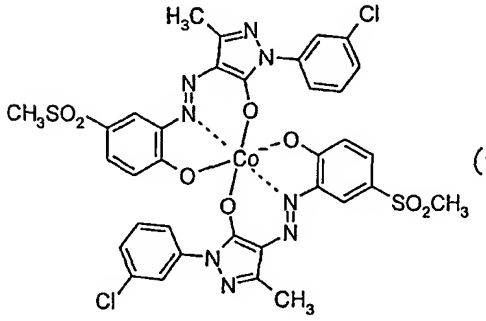
and tautomers thereof, r is a number from 1 to 6, s is a number from 1 to 4, and Q^- is an organometallic anion selected from the group consisting of



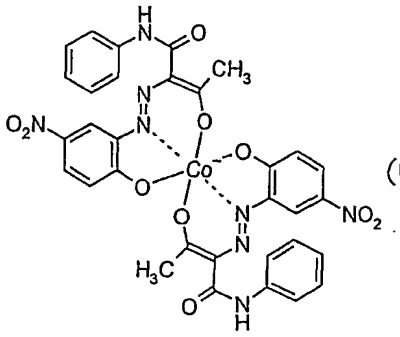
(Q1),



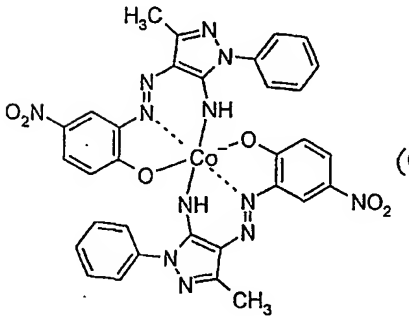
(Q2),



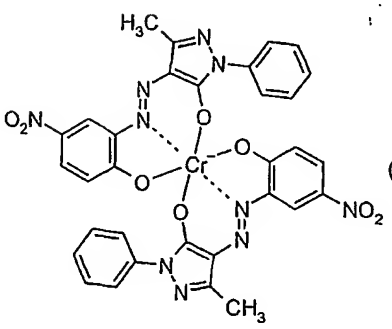
(Q3),



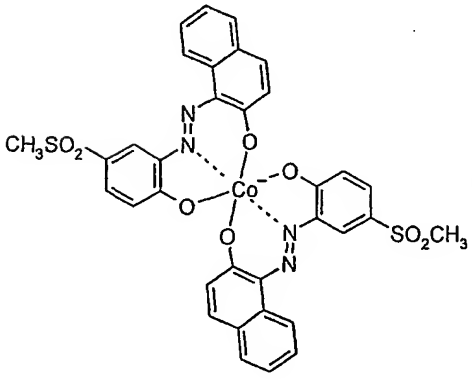
(Q4),



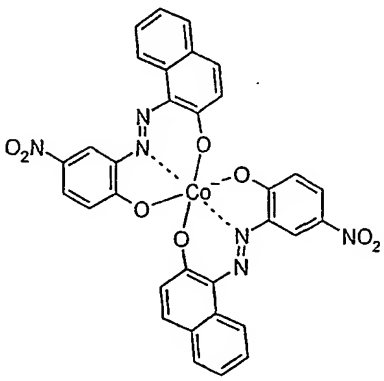
(Q5),



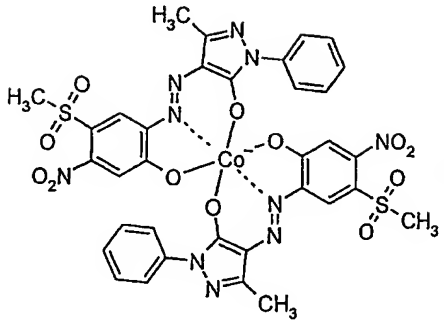
(Q6),



(Q7),



(Q8),



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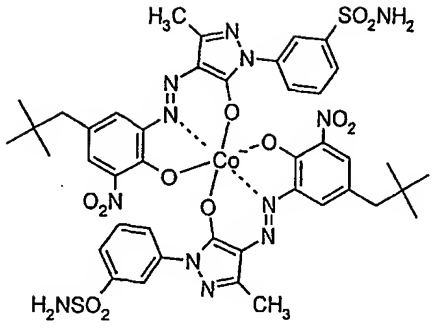

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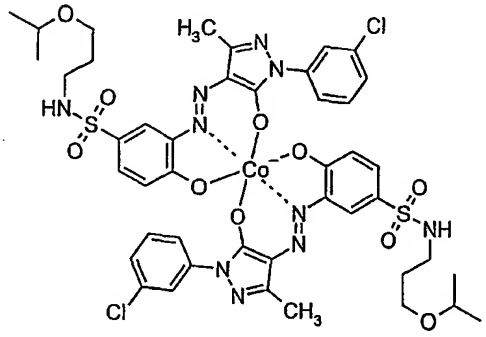

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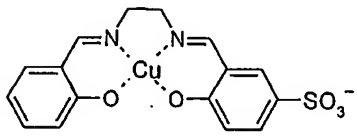
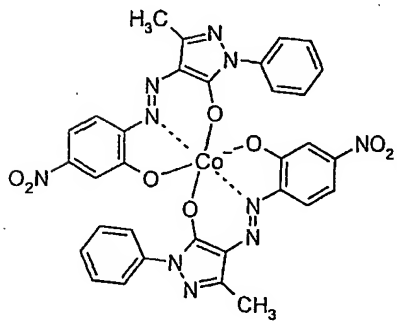


(Q12),



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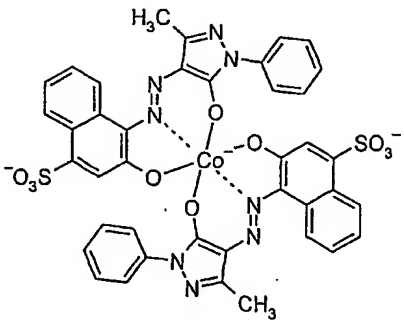

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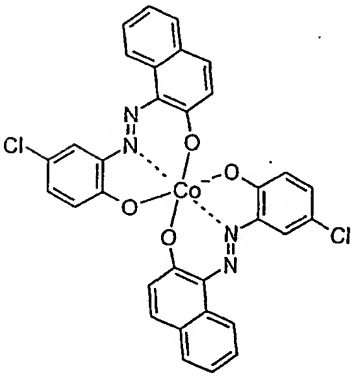

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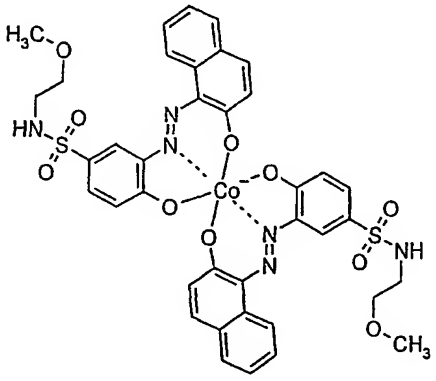

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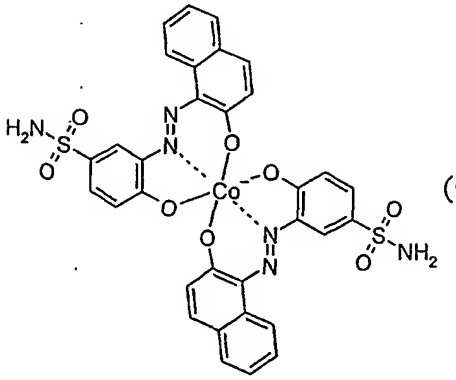

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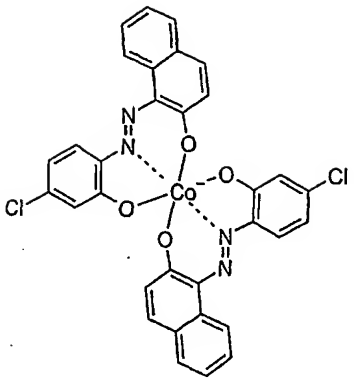

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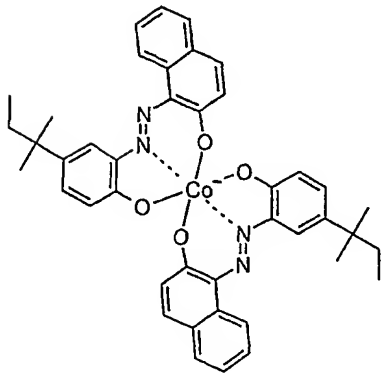

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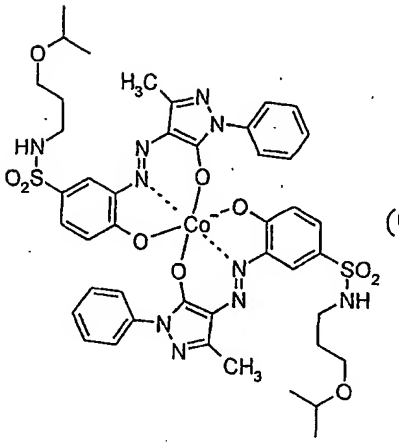

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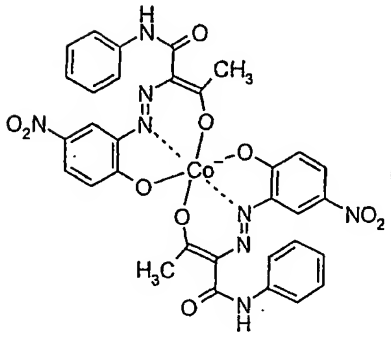

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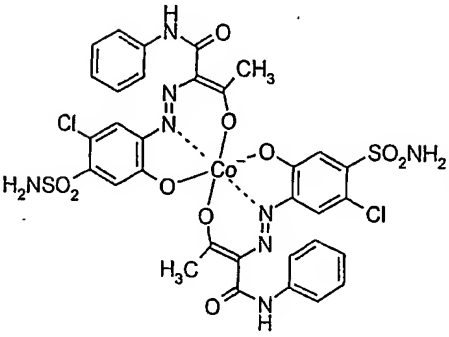

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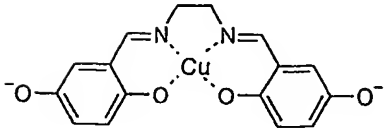

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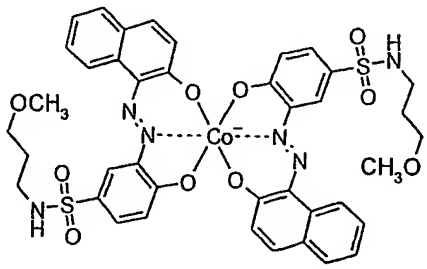

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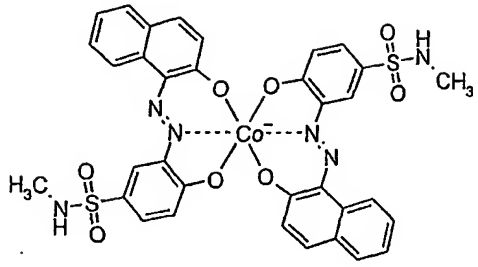

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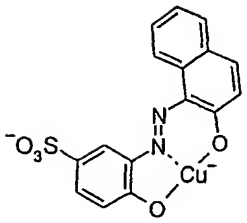

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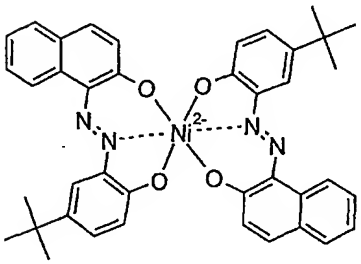

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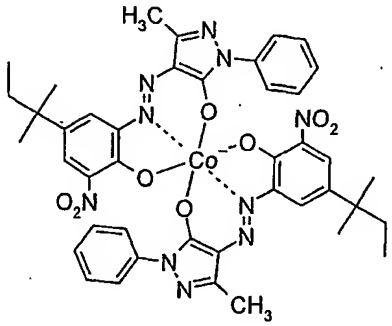

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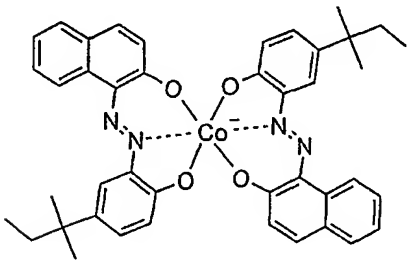

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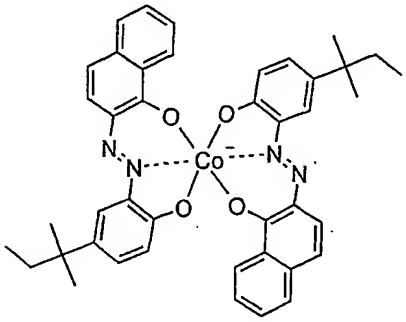

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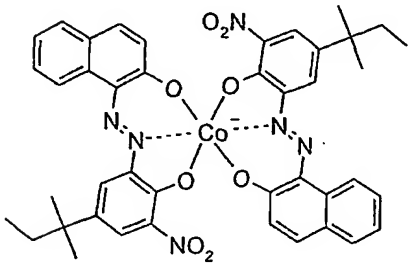

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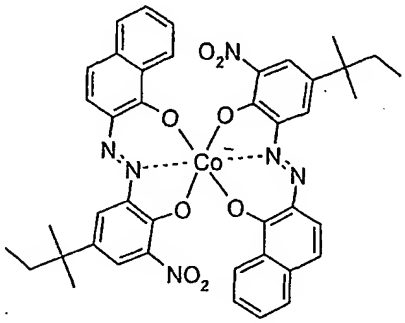

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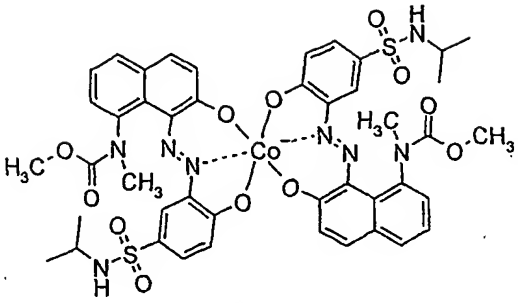

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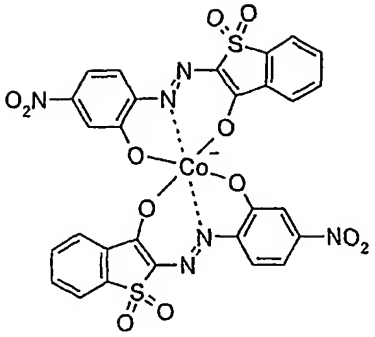

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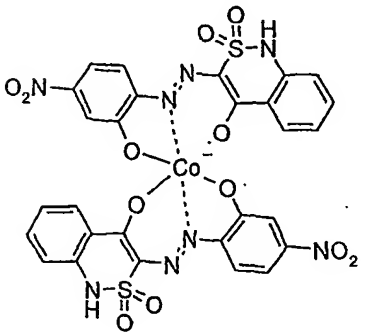

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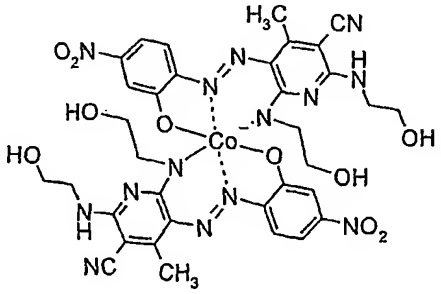

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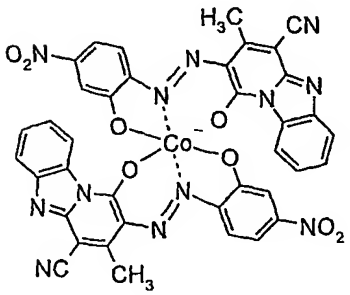

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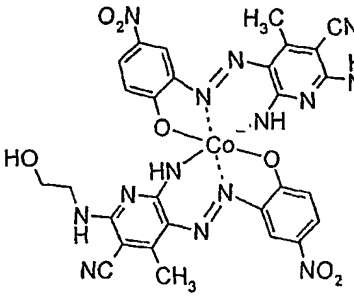

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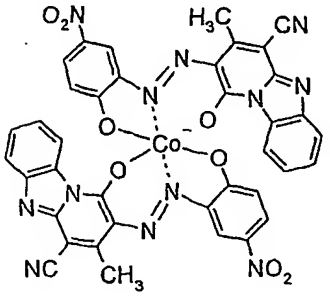

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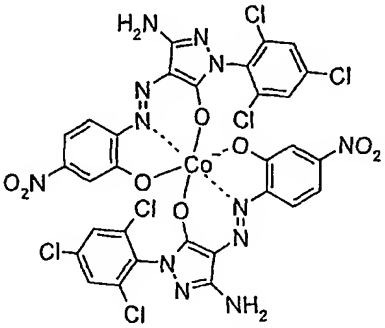

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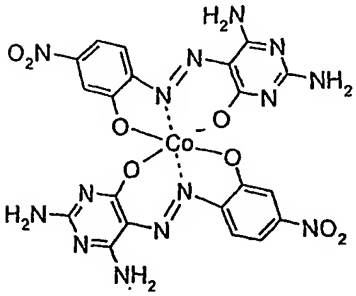

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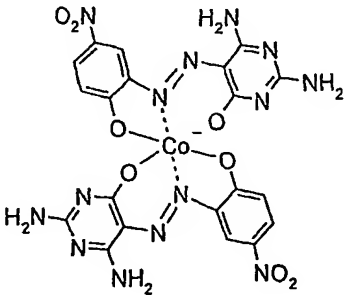

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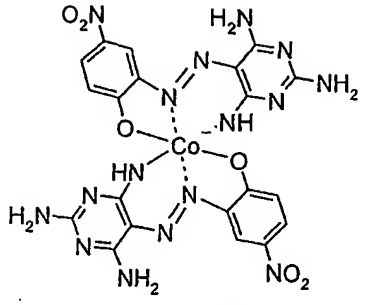
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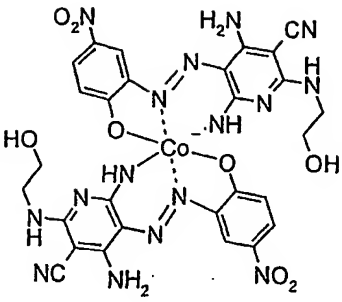
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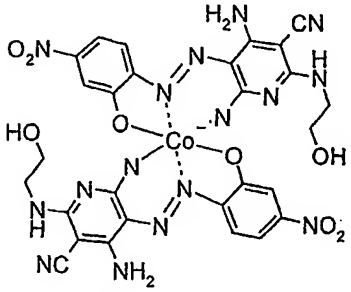
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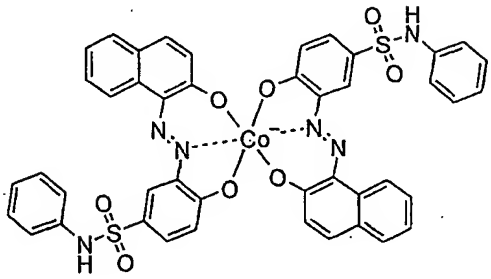
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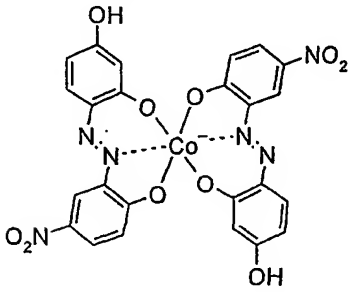
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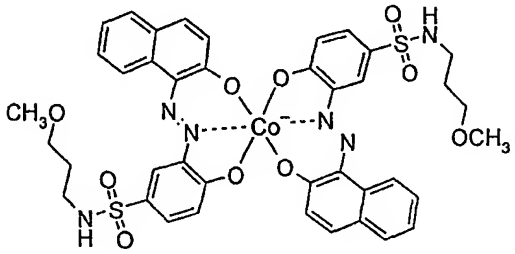
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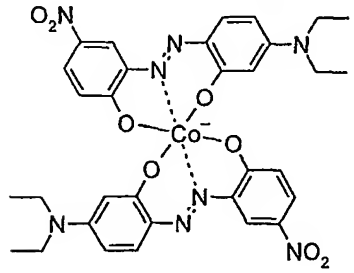
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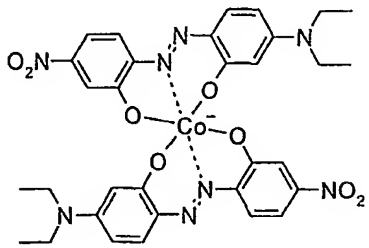
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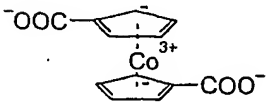
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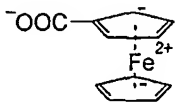
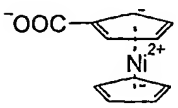
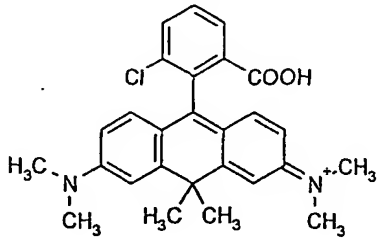
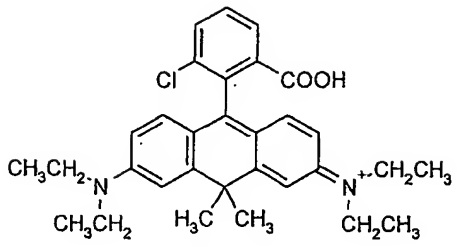

(Q52) and


(Q53).

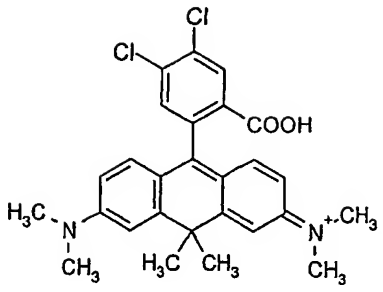
In formula (VI), preferably r is 0 and s is 1 or 2, or especially r is 1 and s is 0,

for example compounds wherein G^+ is

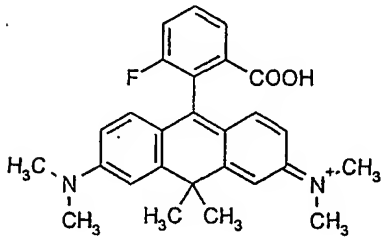

(G84),



(G85),



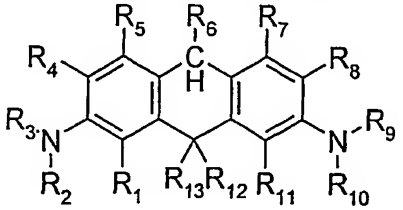
(G86) or



(G87).

The compounds of formulae (I) and (II) are in some cases known compounds which can be found, for example, in the prior art mentioned above. Some of them are new, but they can be prepared analogously to the known compounds by methods known *per se*, for example by methods disclosed in J. Chem. Soc. III 1963 / 2655-2662, J. Chem. Soc. (B) 1967 / 91-92, J. Chem. Soc. (B) 1969 / 1068-1071, J. Chem. Soc. (B) 1971 / 319-324, J. Chem. Soc. (B) 1971 / 1468-1471 or Heterocycles 21/1, 167-190 [1984]. The compounds used according to the invention can also be prepared from their leuco forms, some of which are known for photographic and electrophotographic applications, according to methods known to the person skilled in the art. Metal complexes, preferably those of formula (III), are well known from the specialist literature. In particular, they may be those metal complexes described in GB 1 599 812 or EP 450 421, and reference is made expressly to the teaching contained therein.

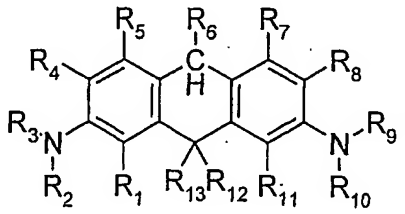
Compounds of formula (I) or their precursors are preferably prepared by oxidation of a compound of formula



(X), it having been found, most surprisingly, that liquid acids, for example acetic acid, are especially advantageous solvents and (meta)periodate is an especially advantageous oxidising agent, especially in combination. The reaction

proceeds more selectively and the compounds in question are obtained in better yield and better purity, which results in better application-related properties in optical storage media. Ammonium (meta)periodates, especially tetrabutylammonium (meta)periodate, and acetic acid, especially glacial acetic acid, are particularly advantageous.

The invention accordingly relates also to a process for the preparation of a compound of formula (I), wherein a compound of structure



(X)

is oxidised in the presence of a C_1-C_{18}carboxylic acid. The amount of C_1-C_{18}carboxylic acid is advantageously from 0.1 to 10 000 parts by weight, based on (X).

The carbopyronine dyes used according to the invention have in ethanolic solution a narrow absorption band having its maximum at from 540 to 640 nm. Very surprisingly, they also have a comparatively weak tendency towards agglomeration in the solid state, so that the absorption curve remains advantageously narrow also in the solid state. This is true especially in the presence of metal-containing anions $(X^{m-})_p$, for example the metal complex anions indicated above.

The carbopyronine dyes used according to the invention also have, in the form of a solid film, as used in optical storage media, at the longer wavelength flank of the absorption band a high refractive index which preferably achieves a peak value of from 2.0 to 3.0 in the range of from 600 to 700 nm, so that a medium having high reflectivity as well as high sensitivity and good playback characteristics in the desired spectral range is achieved.

The substrate, which functions as support for the layers applied thereto, is advantageously semi-transparent ($T \geq 10\%$) or preferably transparent ($T \geq 90\%$). The support can have a thickness of from 0.01 to 10 mm, preferably from 0.1

to 5 mm.

The recording layer is preferably arranged between the transparent substrate and the reflecting layer. The thickness of the recording layer is from 10 to 1000 nm, preferably from 30 to 300 nm, especially about 80 nm, for example from 60 to 120 nm. The absorption of the recording layer is typically from 0.1 to 1.0 at the absorption maximum. The layer thickness is very especially chosen in known manner depending upon the respective refractive indices in the non-written state and in the written state at the reading wavelength, so that in the non-written state constructive interference is obtained, but in the written state destructive interference is obtained, or *vice versa*.

The reflecting layer, the thickness of which can be from 10 to 150 nm, preferably has high reflectivity ($R \geq 45\%$, especially $R \geq 60\%$), coupled with low transparency ($T \leq 10\%$). In further embodiments, for example in the case of media having a plurality of recording layers, the reflector layer may likewise be semi-transparent, that is to say may have comparatively high transparency (for example $T \geq 50\%$) and low reflectivity (for example $R \leq 30\%$).

The uppermost layer, for example the reflective layer or the recording layer, depending upon the layer structure, is advantageously additionally provided with a protective layer having a thickness of from 0.1 to 1000 μm, preferably from 0.1 to 50 μm, especially from 0.5 to 15 μm. Such a protective layer can, if desired, serve also as adhesion promoter for a second substrate layer applied thereto, which is preferably from 0.1 to 5 mm thick and consists of the same material as the support substrate.

The reflectivity of the entire recording medium is preferably at least 15%, especially at least 40%.

The main features of the recording layer according to the invention are the very high initial reflectivity in the said wavelength range of the laser diodes, which can be modified with especially high sensitivity; the high refractive index; the narrow absorption band in the solid state; the good uniformity of the script width at different pulse durations; the good light stability; and the good solubility in polar solvents.

The recording medium according to the invention is neither writable nor readable using the infra-red laser diodes of customary CD apparatus in accordance with the requirements of the Orange Book Standard, because at 780 nm the refractive indices (n) characteristically lie between 1.4 and 1.9 and their imaginary components (k) between 0 and a maximum of 0.04. As a result, the risk of damage in the event of an erroneous attempt at writing using an apparatus not capable of high resolution is largely averted, which is of advantage. The use of dyes of formula (I) results in advantageously homogeneous, amorphous and low-scatter recording layers having a high refractive index, and the absorption edge is surprisingly especially steep even in the solid phase. Further advantages are high light stability in daylight and under laser radiation of low power density with, at the same time, high sensitivity under laser radiation of high power density, uniform script width, high contrast, and also good thermal stability and storage stability.

At a relatively high recording speed, the results obtained are surprisingly better than with previously known recording media. The marks are more precisely defined relative to the surrounding medium, and thermally induced deformations do not occur. The error rate (BLER) and the statistical variations in mark length (jitter) are also low both at normal recording speed and at relatively high recording speed, so that an error-free recording and playback can be achieved over a large speed range. There are virtually no rejects even at high recording speed, and the reading of written media is not slowed down by the correction of errors. The advantages are obtained in the entire range of from 600 to 700 nm (preferably from 630 to 690 nm), but are especially marked at from 640 to 680 nm, more especially from 650 to 670 nm, particularly at 658 ± 5 nm.

Suitable substrates are, for example, glass, minerals, ceramics and thermosetting or thermoplastic plastics. Preferred supports are glass and homo- or co-polymeric plastics. Suitable plastics are, for example, thermoplastic polycarbonates, polyamides, polyesters, polyacrylates and polymethacrylates, polyurethanes, polyolefins, polyvinyl chloride, polyvinylidene fluoride, polyimides, thermosetting polyesters and epoxy resins. The substrate can be in pure form or may also comprise customary additives, for example UV absorbers or dyes, as proposed e.g. in JP 04/167 239 as light-stabilisers for

the recording layer. In the latter case it may be advantageous for the dye added to the support substrate to have an absorption maximum hypsochromically shifted relative to the dye of the recording layer by at least 10 nm, preferably by at least 20 nm.

The substrate is advantageously transparent over at least a portion of the range from 600 to 700 nm (preferably as indicated above), so that it is permeable to at least 90% of the incident light of the writing or readout wavelength. The substrate has preferably on the coating side a spiral guide groove having a groove depth of from 50 to 500 nm, a groove width of from 0.2 to 0.8 μm and a track spacing between two turns of from 0.4 to 1.6 μm, especially having a groove depth of from 100 to 200 nm, a groove width of 0.3 μm and a spacing between two turns of from 0.6 to 0.8 μm. The storage media according to the invention are therefore suitable especially advantageously for the optical recording of DVD media having the currently customary pit width of 0.4 μm and track spacing of 0.74 μm. The increased recording speed relative to known media allows synchronous recording or, for special effects, even accelerated recording of video sequences with excellent image quality.

The recording layer, instead of comprising a single compound of formula (I) or (II), may also comprise a mixture of such compounds having, for example, 2, 3, 4 or 5 carbopyronine dyes according to the invention. By the use of mixtures, for example mixtures of isomers or homologues as well as mixtures of different structures, the solubility can often be increased and/or the amorphous content improved. If desired, mixtures of ion pair compounds may have different anions, different cations or both different anions and different cations.

For a further increase in stability it is also possible, if desired, to add known stabilisers in customary amounts, for example a nickel dithiolate described in JP 04/025 493 as light stabiliser.

The recording layer comprises a compound of formula (I) or (II) or a mixture of such compounds advantageously in an amount sufficient to have a substantial influence on the refractive index, for example at least 30% by weight, preferably at least 60% by weight, especially at least 80% by weight. The recording layer can especially valuably comprise a compound of formula (I) or a mixture

of a plurality of such compounds as main component, or may consist exclusively or substantially of one or more compounds of formula (I).

Further customary constituents are possible, for example other chromophores (for example those disclosed in WO-01/75873, or others having an absorption maximum at from 300 to 1000 nm), stabilisers, $^1O_2$-, triplet- or luminescence-quenchers, melting-point reducers, decomposition accelerators or any other additives that have already been described in optical recording media. Preferably, stabilisers or fluoresence-quenchers are added if desired.

When the recording layer comprises further chromophores, they may in principle be any dye that can be decomposed or modified by the laser radiation during the recording, or they may be inert towards the laser radiation. When the further chromophores are decomposed or modified by the laser radiation, this can take place directly by absorption of the laser radiation or can be induced indirectly by the decomposition of the compounds of formula (I) or (II) according to the invention, for example thermally.

Naturally, further chromophores or coloured stabilisers may influence the optical properties of the recording layer. It is therefore preferable to use further chromophores or coloured stabilisers, the optical properties of which conform as far as possible to those of the compounds formula (I) or (II) or are as different as possible, or the amount of further chromophores is kept small.

When further chromophores having optical properties that conform as far as possible to those of compounds formula (I) or (II) are used, preferably this should be the case in the range of the longest-wavelength absorption flank. Preferably the wavelengths of the inversion points of the further chromophores and of the compounds of formula (I) or (II) are a maximum of 20 nm, especially a maximum of 10 nm, apart. In that case the further chromophores and the compounds of formula (I) or (II) should exhibit similar behaviour in respect of the laser radiation, so that it is possible to use as further chromophores known recording agents the action of which is synergistically enhanced or heightened by the compounds of formula (I) or (II).

When further chromophores or coloured stabilisers having optical properties that are as different as possible from those of compounds of formula (I) or (II)

are used, they advantageously have an absorption maximum that is hypsochromically or bathochromically shifted relative to the dye of formula (I) or (II). In that case the absorption maxima are preferably at least 50 nm, especially at least 100 nm, apart. Examples thereof are UV absorbers that are hypsochromic to the dye of formula (I) or (II), or coloured stabilisers that are bathochromic to the dye of formula (I) or (II) and have absorption maxima lying, for example, in the NIR or IR range. Other dyes can also be added for the purpose of colour-coded identification, colour-masking ("diamond dyes") or enhancing the aesthetic appearance of the recording layer. In all those cases, the further chromophores or coloured stabilisers should preferably exhibit behaviour towards light and laser radiation that is as inert as possible.

When another dye is added in order to modify the optical properties of the compounds of formula (I) or (II), the amount thereof is dependent upon the optical properties to be achieved. The person skilled in the art will find little difficulty in varying the ratio of additional dye to compound of formula (I) or (II) until he obtains his desired result.

When chromophores or coloured stabilisers are used for other purposes, the amount thereof should preferably be small so that their contribution to the total absorption of the recording layer in the range of from 600 to 700 nm is a a maximum of 20%, preferably a maximum of 10%. In such a case, the amount of additional dye or stabiliser is advantageously a maximum of 50% by weight, preferably a maximum of 10% by weight, based on the recording layer.

Most preferably, however, no additional chromophore is added, unless it is a coloured stabiliser.

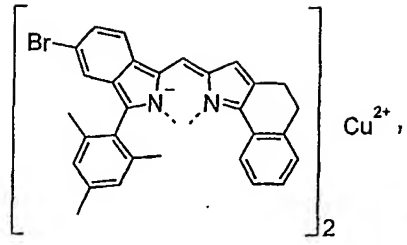
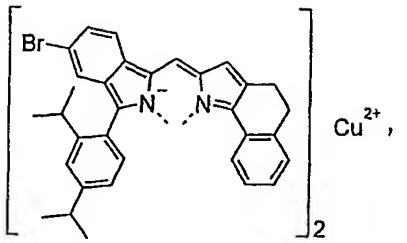
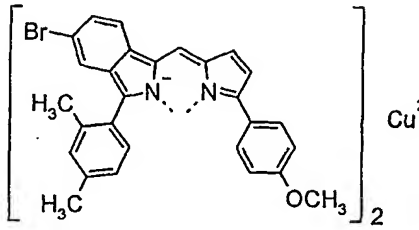
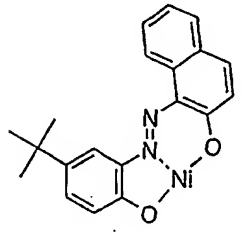
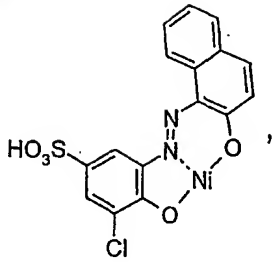
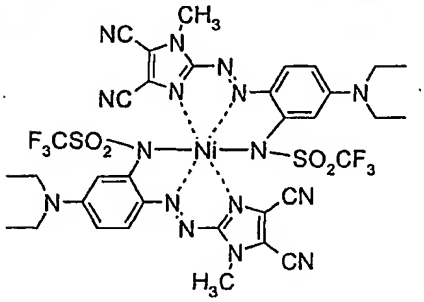
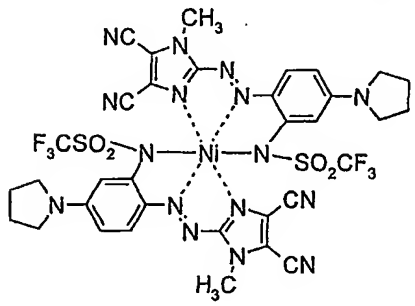
Further chromophores that can be used in the recording layer in addition to the compounds of formula (I) or (II) are, for example, cyanines and cyanine metal complexes (US 5 958 650), styryl compounds (US-6 103 331), oxonol dyes (EP-A-833 314), azo dyes and azo metal complexes (JP-A-11/028865), phthalocyanines (EP-A-232 427, EP-A-337 209, EP-A-373 643, EP-A-463 550, EP-A-492 508, EP-A-509 423, EP-A-511 590, EP-A-513 370, EP-A-514 799, EP-A-518 213, EP-A-519 419, EP-A-519 423, EP-A-575 816, EP-A-600 427, EP-A-676 751, EP-A-712 904, WO-98/14520, WO-00/09522, PCT/EP-02/03945), porphyrins and azaporphyrins (EP-A-822 546, US-5 998 093),

dipyrromethene dyes and metal chelate compounds thereof (EP-A-822 544, EP-A-903 733), xanthene dyes and metal complex salts thereof (US-5 851 621) or quadratic acid compounds (EP-A-568 877), or oxazines, dioxazines, diaza-styryls, formazans, anthraquinones or phenothiazines; this list is on no account exhaustive and the person skilled in the art will interpret the list as including further known dyes.

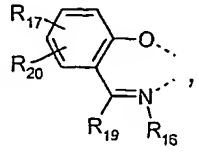
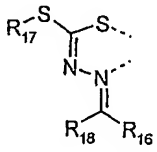
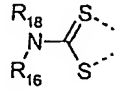
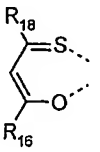
Stabilisers, $^1O_2$-, triplet- or luminescence-quenchers are, for example, metal complexes of N- or S-containing enolates, phenolates, bisphenolates, thiolates or bisthiolates or of azo, azomethine or formazan dyes, such as bis(4-dimethyl-aminodithiobenzil)nickel [CAS N° 38465-55-3], ®Irgalan Bordeaux EL, ®Cibafast N or similar compounds, hindered phenols and derivatives thereof (optionally also as counter-ions X), such as ®Cibafast AO, o-hydroxyphenyl-triazoles or -triazines or other UV absorbers, such as ®Cibafast W or ®Cibafast P or hindered amines (TEMPO or HALS, also as nitroxides or NOR-HALS, optionally also as counter-ions X), and also as cations diimmonium, Paraquat™ or Orthoquat™ salts, such as ®Kayasorb IRG 022, ®Kayasorb IRG 040, optionally also as radical ions, such as N,N,N',N'-tetrakis(4-dibutylaminophenyl)-p-phenylene-amine-ammonium hexafluorophosphate, hexafluoroantimonate or perchlorate. The latter are available from Organica (Wolfen / DE); ®Kayasorb brands are available from Nippon Kayaku Co. Ltd., and ®Irgalan and ®Cibafast brands are available from Ciba Spezialitätenchemie AG.

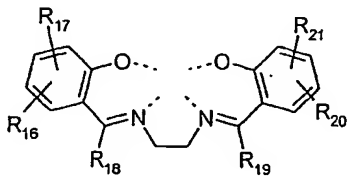
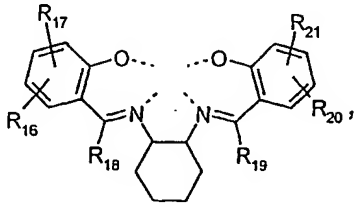
Many such structures are known, some of them also in connection with optical recording media, for example from US-5 219 707, JP-A-06/199045, JP-A-07/76169, JP-A-07/262604 or JP-A-2000/272241. They may be, for example, salts of the metal complex anions disclosed above with any desired cations, for example the cations disclosed above.

Also suitable are neutral metal complexes, for example those metal complexes disclosed in EP 0 822 544, EP 0 844 243, EP 0 903 733, EP 0 996 123, EP 1 056 078, EP 1 130 584 or US 6 162 520, for example

, and also those of the formula $(L_3)M_2(L_5)$ (VII), $(L_6)M_2(L_7)$ (VIII) or $M_2(L_8)$ (IX), wherein L_5 is C_1-C_{12}alkyl-OH, C_6-C_{12}aryl-OH, C_7-C_{12}aralkyl-OH, C_1-C_{12}alkyl-SH, C_6-C_{12}aryl-SH, C_7-C_{12}aralkyl-SH, C_1-C_{12}alkyl-NH_2, C_6-C_{12}aryl-NH_2, C_7-C_{12}aralkyl-NH_2, di-C_1-C_{12}alkyl-NH, di-C_6-C_{12}aryl-NH, di-C_7-C_{12}aralkyl-NH, tri-C_1-C_{12}alkyl-N, tri-C_6-C_{12}aryl-N or tri-C_7-C_{12}aralkyl-N,

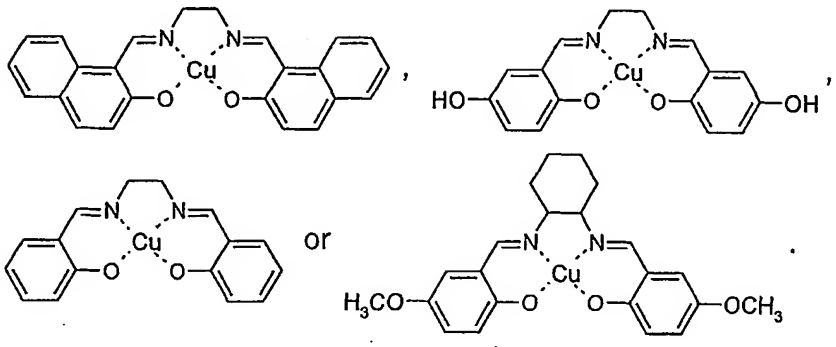
L_6 and L_7 are  ,  ,  or  , and

L_8 is  or  ,

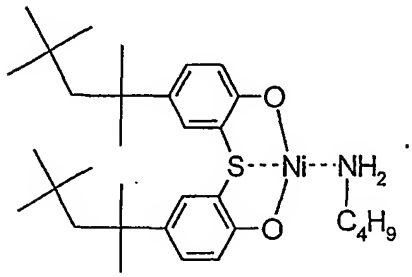
M_2 and R_{16} to R_{21} being as defined above.

A particular example of an additive of formula (IX) that may be mentioned is a

copper complex, illustrated e.g. by a compound of formula



A particular example of an additive of formula (VII) that may be mentioned is a nickel bisphenolate, illustrated e.g. by the compound of formula



The person skilled in the art will know from other optical information media, or will easily identify, which additives in which concentration are best suited to which purpose. Suitable concentrations of additives are, for example, from 0.001 to 1000% by weight, preferably from 1 to 50% by weight, based on the recording medium of formula (I) or (II).

The recording medium according to the invention, in addition to comprising compounds of formula (I) or (II), may additionally comprise salts, for example ammonium chloride, pentadecylammonium chloride, sodium chloride, sodium sulfate, sodium methyl sulfonate or sodium methyl sulfate, the ions of which may originate e.g. from the components used. The additional salts, if present, may be present preferably in amounts of up to 20% by weight, based on the total weight of the recording layer.

Reflecting materials suitable for the reflective layer include especially metals, which provide good reflection of the laser radiation used for recording and

playback, for example the metals of Main Groups III, IV and V and of the Sub-Groups of the Periodic Table of the Elements. Al, In, Sn, Pb, Sb, Bi, Cu, Ag, Au, Zn, Cd, Hg, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and alloys thereof are especially suitable. Special preference is given to a reflective layer of aluminium, silver, copper, gold or an alloy thereof, on account of their high reflectivity and ease of production.

Materials suitable for the protective layer include chiefly plastics, which are applied in a thin layer to the support or the uppermost layer either directly or with the aid of adhesive layers. It is advantageous to select mechanically and thermally stable plastics having good surface properties, which may be modified further, for example written. The plastics may be thermosetting plastics and thermoplastic plastics. Preference is given to radiation-cured (e.g using UV radiation) protective layers, which are particularly simple and economical to produce. A wide variety of radiation-curable materials are known. Examples of radiation-curable monomers and oligomers are acrylates and methacrylates of diols, triols and tetrols, polyimides of aromatic tetra-carboxylic acids and aromatic diamines having C_1-C_4alkyl groups in at least two ortho-positions of the amino groups, and oligomers with dialkylmaleinimidyl groups, e.g. dimethylmaleinimidyl groups.

The recording media according to the invention may also have additional layers, for example interference layers. It is also possible to construct recording media having a plurality of (for example two) recording layers. The structure and the use of such materials are known to the person skilled in the art. Preferred, if present, are interference layers that are arranged between the recording layer and the reflecting layer and/or between the recording layer and the substrate and consist of a dielectric material, for example as described in EP 353 393 of TiO_2, Si_3N_4, ZnS or silicone resins.

The recording media according to the invention can be produced by processes known *per se*, various methods of coating being employable depending upon the materials used and their function.

Suitable coating methods are, for example, immersion, pouring, brush-coating, blade-application and spin-coating, as well as vapour-deposition methods

carried out under a high vacuum. When pouring methods are used, for example, solutions in organic solvents are generally used. When solvents are employed, care should be taken that the supports used are insensitive to those solvents. Suitable coating methods and solvents are described, for example, in EP-A-401 791.

The recording layer is preferably applied by spin-coating with a dye solution, solvents that have proved satisfactory being especially alcohols, e.g. 2-methoxyethanol, n-propanol, isopropanol, isobutanol, n-butanol, amyl alcohol or 3-methyl-1-butanol or preferably fluorinated alcohols, e.g. 2,2,2-trifluoro-ethanol or 2,2,3,3-tetrafluoro-1-propanol, and mixtures thereof. It will be understood that other solvents or solvent mixtures can also be used, for example those solvent mixtures described in EP-A-511 598 and EP-A-833 316. Ethers (dibutyl ether), ketones (2,6-dimethyl-4-heptanone, 5-methyl-2-hexanone) or saturated or unsaturated hydrocarbons (toluene, xylene) can also be used, for example in the form of mixtures (e.g. dibutyl ether / 2,6-dimethyl-4-heptanone) or mixed components.

The person skilled in the art of spin-coating will in general routinely try out all the solvents with which is he is familiar, as well as binary and ternary mixtures thereof, in order to discover the solvents or solvent mixtures which result in a high-quality and, at the same time, cost-effective recording layer containing the solid components of his choice. Known methods of process engineering can also be employed in such optimisation procedures, so that the number of experiments to be carried out can be kept to a minimum.

The invention therefore relates also to a method of producing an optical recording medium, wherein a solution of a compound of formula (I) in an organic solvent is applied to a substrate having pits. The application is preferably carried out by spin-coating.

The application of the metallic reflective layer is preferably effected by sputtering, vapour-deposition *in vacuo* or by chemical vapour deposition (CVD). The sputtering technique is especially preferred for the application of the metallic reflective layer on account of the high degree of adhesion to the support. Such techniques are known and are described in specialist literature (e.g. J.L. Vossen and W. Kern, "Thin Film Processes", Academic Press, 1978).

The structure of the recording medium according to the invention is governed primarily by the readout method; known function principles include the measurement of the change in the transmission or, preferably, in the reflection, but it is also known to measure, for example, the fluorescence instead of the transmission or reflection.

When the recording material is structured for a change in reflection, the following structures, for example, can be used: transparent support / recording layer (optionally multilayered) / reflective layer and, if expedient, protective layer (not necessarily transparent); or support (not necessarily transparent) / reflective layer / recording layer and, if expedient, transparent protective layer. In the first case, the light is incident from the support side, whereas in the latter case the radiation is incident from the recording layer side or, where applicable, from the protective layer side. In both cases the light detector is located on the same side as the light source. The first-mentioned structure of the recording material to be used according to the invention is generally preferred.

When the recording material is structured for a change in light transmission, the following different structure, for example, comes into consideration: transparent support/ recording layer (optionally multilayered) and, if expedient, transparent protective layer. The light for recording and for readout can be incident either from the support side or from the recording layer side or, where applicable, from the protective layer side, the light detector in this case always being located on the opposite side.

Suitable lasers are those having a wavelength of 600-700 nm, for example commercially available lasers having a wavelength of 602, 612, 633, 635, 647, 650, 670 or 680 nm, especially semi-conductor lasers, such as GaAsAl, InGaAlP or GaAs laser diodes having a wavelength especially of about 635, 650 or 658 nm. The recording is effected, for example, point for point in a manner known *per se*, by modulating the laser in accordance with the mark lengths and focussing its radiation onto the recording layer. It is known from the specialist literature that other methods are currently being developed which may also be suitable for use.

The process according to the invention allows the storage of information with

great reliability and stability, distinguished by very good mechanical and thermal stability and by high light stability and by sharp boundary zones of the pits. Special advantages include the high contrast, the low jitter and the surprisingly high signal/noise ratio, so that excellent readout is achieved. The high storage capacity is especially valuable in the field of video.

The readout of information is carried out according to methods known *per se* by registering the change in absorption or reflection using laser radiation, for example as described in "CD-Player und R-DAT Recorder" (Claus Biaesch-Wiepke, Vogel Buchverlag, Würzburg 1992).

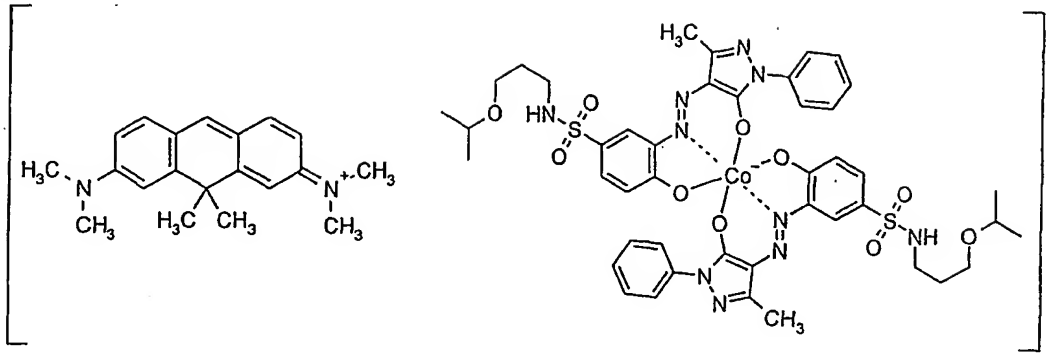
The information-containing medium according to the invention is especially an optical information material of the WORM type. It may be used, for example, as a playable DVD (digital versatile disk), as storage material for a computer or as an identification and security card or for the production of diffractive optical elements, for example holograms.

The invention accordingly relates also to a method for the optical recording, storage and playback of information, wherein a recording medium according to the invention is used. The recording and the playback advantageously take place in a wavelength range of from 600 to 700 nm.

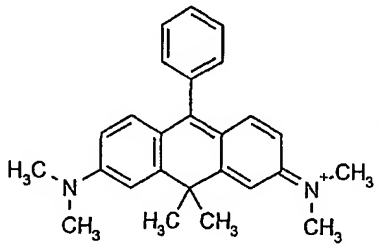
The following Examples illustrate the invention in greater detail:

Example 1 : 98.22 g of N-[7-(dimethylamino)-9,9-dimethyl-2(9H)-anthracenyl-idene]-N-methyl-perchlorate are dissolved in 25 litres of ethanol. Separately, 256.25 g of the sodium salt of the metal complex of formula Q20 (in each case based on dry weight) are then dissolved in 40 litres of ethanol, with heating to 65°C. After cooling to 23°C, the two solutions are combined (for example by pumping the second solution into the first), stirred for 30 minutes to complete the reaction and clarified by filtration. The solution is concentrated by evaporation under a low vacuum using a rotary evaporator with a water bath at a temperature of about 65°C, yielding 353.63 g of crude product. 15 litres of water are added to the crude product and the mixture is treated mechanically and/or by ultrasound for 30 minutes at 10-20°C in order to dissolve the inorganic salts. After filtration and washing with 10 litres of water, the filtration residue is dried at 80°C / $1.6 \cdot 10^3$ Pa , yielding 322.30 g of the

product of formula

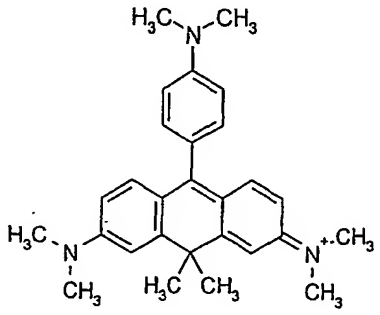


Example 2 : The procedure is as in Example 1, but instead of N-[7-(dimethyl-amino)-9,9-dimethyl-2(9H)-anthracenylidene]-N-methyl-perchlorate there is used an equimolar amount of the product of formula



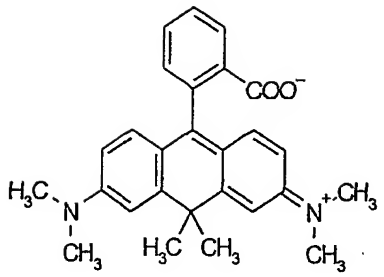
(G11).

Example 3 : The procedure is as in Example 1, but instead of N-[7-(dimethyl-amino)-9,9-dimethyl-2(9H)-anthracenylidene]-N-methyl-perchlorate there is used an equimolar amount of the product of formula



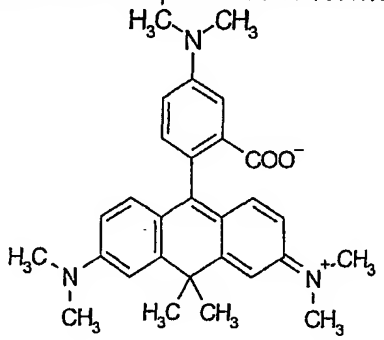
(G88).

Example 4 : The procedure is as in Example 1, but instead of N-[7-(dimethyl-amino)-9,9-dimethyl-2(9H)-anthracenylidene]-N-methyl-perchlorate there is used an equimolar amount of the product of formula



(G89).

Example 5 : The procedure is as in Example 1, but instead of N-[7-(dimethyl-amino)-9,9-dimethyl-2(9H)-anthracenylidene]-N-methyl-perchlorate there is used an equimolar amount of the product of formula



(G90).

Example 6 : The procedure is as in Example 1, but instead of the metal complex of formula Q20 there is used an equimolar amount of the metal complex of formula Q3.

Example 7 : 2% by weight of the product according to Example 1 are dissolved in 2,2,3,3-tetrafluoro-1-propanol and the solution is filtered through a Teflon filter of pore size 0.2 μm and applied by spin-coating at 1000 rev/min to the surface of a 0.6 mm thick, grooved polycarbonate disc (groove depth: 170 nm, groove width: 350 nm, track spacing: 0.74 μm) of 120 mm diameter. The excess solution is spun off by increasing the rotational speed. On evaporation of the solvent, the dye remains behind in the form of a uniform, amorphous solid layer. After drying in a circulating-air oven at 70°C (10 min), the solid layer exhibits an absorption of 0.45 at 625 nm. In a vacuum coating apparatus (Twister™, Balzers Unaxis), a 60 nm thick silver layer is then applied to the recording layer by atomisation. Then a 6 μm thick protective layer of a UV-curable photopolymer (650-020, DSM) is applied thereto by means of spin-coating. The recording support exhibits a reflectivity of 47% at 658 nm. The optical constants (absorption maximum λ_{max}, refractive index at 658 nm n_{658},

absorption coefficient at 658 nm k_{658}) are determined reflectometrically (ETA-RT™, ETA-Optik Steag-Hamatech):

$$\lambda_{max} = 624 \text{ nm} ; n_{658} = 2.29 ; k_{658} = 0.21 .$$

Using a commercial test apparatus (DVDT-R 650™, Expert Magnetics), marks are written into the active layer at a speed of 3.5 m/sec using a laser diode of wavelength 658 nm and laser power of 9.2 mW. Then, using the same test apparatus, the dynamic parameters are determined, there being obtained good measured values:

$$\text{DTC Jitter} = 8.8\% ; R14H = 47\% ; I14/I14H = 0.72 .$$

Example 8 : The procedure is as in Example 7, but the product according to Example 6 is used instead of the product according to Example 1. The optical constants are determined reflectometrically as in Example 7:

$$\lambda_{max} = 626 \text{ nm} ; n_{658} = 2.55 ; k_{658} = 0.33 .$$

Comparison Example 9 : The procedure is as in Examples 7 and 8, but the product according to Example A8 of EP-A-0 805 441 is used instead of the products according to Examples 1 and 6. The optical constants are determined reflectometrically in the same way:

$$\lambda_{max} = 581 \text{ nm} ; n_{658} = 1.94 ; k_{658} = 0.016 .$$

This disc cannot be written using commercial recording apparatus (Pioneer A03 DVD-R(G)) on account of insufficient sensitivity.

Examples 10-2094 : The procedure is as in Examples 7-9, but the following compounds of formula $[G^+] \cdot [X^-]$, which can be prepared analogously to Examples 1-6, are used:

Ex.	$[G^+]$	$[X^-]$
10	G1	Q2
11	G2	Q2
12	G3	Q2
13	G4	Q2
14	G5	Q2
15	G6	Q2
16	G7	Q2
17	G8	Q2
18	G9	Q2
19	G10	Q2
20	G11	Q2
21	G12	Q2
22	G13	Q2
23	G14	Q2
24	G15	Q2
25	G16	Q2
26	G17	Q2
27	G18	Q2
28	G19	Q2
29	G20	Q2
30	G21	Q2
31	G22	Q2
32	G23	Q2
33	G24	Q2
34	G25	Q2
35	G26	Q2
36	G27	Q2
37	G28	Q2
38	G29	Q2

39	G30	Q2
40	G31	Q2
41	G32	Q2
42	G33	Q2
43	G34	Q2
44	G35	Q2
45	G36	Q2
46	G37	Q2
47	G38	Q2
48	G39	Q2
49	G40	Q2
50	G41	Q2
51	G42	Q2
52	G43	Q2
53	G44	Q2
54	G45	Q2
55	G46	Q2
56	G47	Q2
57	G48	Q2
58	G49	Q2
59	G50	Q2
60	G51	Q2
61	G52	Q2
62	G53	Q2
63	G54	Q2
64	G55	Q2
65	G56	Q2
66	G57	Q2
67	G58	Q2
68	G59	Q2
69	G60	Q2
70	G61	Q2
71	G62	Q2
72	G63	Q2
73	G64	Q2
74	G65	Q2
75	G66	Q2
76	G67	Q2
77	G68	Q2
78	G69	Q2
79	G70	Q2
80	G71	Q2
81	G72	Q2

82	G73	Q2
83	G74	Q2
84	G75	Q2
85	G76	Q2
86	G77	Q2
87	G78	Q2
88	G79	Q2
89	G80	Q2
90	G81	Q2
91	G82	Q2
92	G83	Q2
93	G84	Q2
94	G85	Q2
95	G86	Q2
96	G87	Q2
97	G2	Q3
98	G3	Q3
99	G4	Q3
100	G5	Q3
101	G6	Q3
102	G7	Q3
103	G8	Q3
104	G9	Q3
105	G10	Q3
106	G11	Q3
107	G12	Q3
108	G13	Q3
109	G14	Q3
110	G15	Q3
111	G16	Q3
112	G17	Q3
113	G18	Q3
114	G19	Q3
115	G20	Q3
116	G21	Q3
117	G22	Q3
118	G23	Q3
119	G24	Q3
120	G25	Q3
121	G26	Q3
122	G27	Q3
123	G28	Q3
124	G29	Q3

125	G30	Q3
126	G31	Q3
127	G32	Q3
128	G33	Q3
129	G34	Q3
130	G35	Q3
131	G36	Q3
132	G37	Q3
133	G38	Q3
134	G39	Q3
135	G40	Q3
136	G41	Q3
137	G42	Q3
138	G43	Q3
139	G44	Q3
140	G45	Q3
141	G46	Q3
142	G47	Q3
143	G48	Q3
144	G49	Q3
145	G50	Q3
146	G51	Q3
147	G52	Q3
148	G53	Q3
149	G54	Q3
150	G55	Q3
151	G56	Q3
152	G57	Q3
153	G58	Q3
154	G59	Q3
155	G60	Q3
156	G61	Q3
157	G62	Q3
158	G63	Q3
159	G64	Q3
160	G65	Q3
161	G66	Q3
162	G67	Q3
163	G68	Q3
164	G69	Q3
165	G70	Q3
166	G71	Q3
167	G72	Q3

168	G73	Q3
169	G74	Q3
170	G75	Q3
171	G76	Q3
172	G77	Q3
173	G78	Q3
174	G79	Q3
175	G80	Q3
176	G81	Q3
177	G82	Q3
178	G83	Q3
179	G84	Q3
180	G85	Q3
181	G86	Q3
182	G87	Q3
183	G1	Q4
184	G2	Q4
185	G3	Q4
186	G4	Q4
187	G5	Q4
188	G6	Q4
189	G7	Q4
190	G8	Q4
191	G9	Q4
192	G10	Q4
193	G11	Q4
194	G12	Q4
195	G13	Q4
196	G14	Q4
197	G15	Q4
198	G16	Q4
199	G17	Q4
200	G18	Q4
201	G19	Q4
202	G20	Q4
203	G21	Q4
204	G22	Q4
205	G23	Q4
206	G24	Q4
207	G25	Q4
208	G26	Q4
209	G27	Q4
210	G28	Q4

211	G29	Q4
212	G30	Q4
213	G31	Q4
214	G32	Q4
215	G33	Q4
216	G34	Q4
217	G35	Q4
218	G36	Q4
219	G37	Q4
220	G38	Q4
221	G39	Q4
222	G40	Q4
223	G41	Q4
224	G42	Q4
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226	G44	Q4
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228	G46	Q4
229	G47	Q4
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240	G58	Q4
241	G59	Q4
242	G60	Q4
243	G61	Q4
244	G62	Q4
245	G63	Q4
246	G64	Q4
247	G65	Q4
248	G66	Q4
249	G67	Q4
250	G68	Q4
251	G69	Q4
252	G70	Q4
253	G71	Q4

254	G72	Q4
255	G73	Q4
256	G74	Q4
257	G75	Q4
258	G76	Q4
259	G77	Q4
260	G78	Q4
261	G79	Q4
262	G80	Q4
263	G81	Q4
264	G82	Q4
265	G83	Q4
266	G84	Q4
267	G85	Q4
268	G86	Q4
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292	G23	Q5
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294	G25	Q5
295	G26	Q5
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297	G28	Q5
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299	G30	Q5
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445	G2	Q7
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448	G5	Q7
449	G6	Q7
450	G7	Q7
451	G8	Q7
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453	G10	Q7
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462	G19	Q7
463	G20	Q7
464	G21	Q7
465	G22	Q7
466	G23	Q7
467	G24	Q7
468	G25	Q7

469	G26	Q7
470	G27	Q7
471	G28	Q7
472	G29	Q7
473	G30	Q7
474	G31	Q7
475	G32	Q7
476	G33	Q7
477	G34	Q7
478	G35	Q7
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487	G44	Q7
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489	G46	Q7
490	G47	Q7
491	G48	Q7
492	G49	Q7
493	G50	Q7
494	G51	Q7
495	G52	Q7
496	G53	Q7
497	G54	Q7
498	G55	Q7
499	G56	Q7
500	G57	Q7
501	G58	Q7
502	G59	Q7
503	G60	Q7
504	G61	Q7
505	G62	Q7
506	G63	Q7
507	G64	Q7
508	G65	Q7
509	G66	Q7
510	G67	Q7
511	G68	Q7

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521	G78	Q7
522	G79	Q7
523	G80	Q7
524	G81	Q7
525	G82	Q7
526	G83	Q7
527	G84	Q7
528	G85	Q7
529	G86	Q7
530	G87	Q7
531	G1	Q8
532	G2	Q8
533	G3	Q8
534	G4	Q8
535	G5	Q8
536	G6	Q8
537	G7	Q8
538	G8	Q8
539	G9	Q8
540	G10	Q8
541	G11	Q8
542	G12	Q8
543	G13	Q8
544	G14	Q8
545	G15	Q8
546	G16	Q8
547	G17	Q8
548	G18	Q8
549	G19	Q8
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1407	G7	Q18
1408	G8	Q18
1409	G9	Q18
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1411	G11	Q18
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1413	G13	Q18
1414	G14	Q18

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1453	G53	Q18
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1784	G38	Q22
1785	G39	Q22
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1795	G49	Q22
1796	G50	Q22
1797	G51	Q22
1798	G52	Q22
1799	G53	Q22
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1801	G55	Q22

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1803	G57	Q22
1804	G58	Q22
1805	G59	Q22
1806	G60	Q22
1807	G61	Q22
1808	G62	Q22
1809	G63	Q22
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1838	G5	Q23
1839	G6	Q23
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1841	G8	Q23
1842	G9	Q23
1843	G10	Q23
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1845	G12	Q23
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1847	G14	Q23
1848	G15	Q23
1849	G16	Q23
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1877	G44	Q23
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1894	G61	Q23
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1896	G63	Q23
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1902	G69	Q23
1903	G70	Q23
1904	G71	Q23
1905	G72	Q23
1906	G73	Q23
1907	G74	Q23
1908	G75	Q23
1909	G76	Q23
1910	G77	Q23
1911	G78	Q23
1912	G79	Q23
1913	G80	Q23
1914	G81	Q23
1915	G82	Q23
1916	G83	Q23
1917	G84	Q23
1918	G85	Q23
1919	G86	Q23
1920	G87	Q23
1921	G1	Q24
1922	G2	Q24
1923	G3	Q24
1924	G4	Q24
1925	G5	Q24
1926	G6	Q24
1927	G7	Q24
1928	G8	Q24
1929	G9	Q24
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1931	G11	Q24
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1933	G13	Q24
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1940	G20	Q24
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1947	G27	Q24
1948	G28	Q24
1949	G29	Q24
1950	G30	Q24
1951	G31	Q24
1952	G32	Q24
1953	G33	Q24
1954	G34	Q24
1955	G35	Q24
1956	G36	Q24
1957	G37	Q24
1958	G38	Q24
1959	G39	Q24
1960	G40	Q24
1961	G41	Q24
1962	G42	Q24
1963	G43	Q24
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1965	G45	Q24
1966	G46	Q24
1967	G47	Q24
1968	G48	Q24
1969	G49	Q24
1970	G50	Q24
1971	G51	Q24
1972	G52	Q24
1973	G53	Q24

1974	G54	Q24
1975	G55	Q24
1976	G56	Q24
1977	G57	Q24
1978	G58	Q24
1979	G59	Q24
1980	G60	Q24
1981	G61	Q24
1982	G62	Q24
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1984	G64	Q24
1985	G65	Q24
1986	G66	Q24
1987	G67	Q24
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1989	G69	Q24
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1991	G71	Q24
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1993	G73	Q24
1994	G74	Q24
1995	G75	Q24
1996	G76	Q24
1997	G77	Q24
1998	G78	Q24
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2002	G82	Q24
2003	G83	Q24
2004	G84	Q24
2005	G85	Q24
2006	G86	Q24
2007	G87	Q24
2008	G1	Q25
2009	G2	Q25
2010	G3	Q25
2011	G4	Q25
2012	G5	Q25
2013	G6	Q25
2014	G7	Q25
2015	G8	Q25
2016	G9	Q25
2017	G10	Q25
2018	G11	Q25
2019	G12	Q25
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2021	G14	Q25
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2026	G19	Q25
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2029	G22	Q25
2030	G23	Q25
2031	G24	Q25
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2034	G27	Q25
2035	G28	Q25
2036	G29	Q25
2037	G30	Q25
2038	G31	Q25
2039	G32	Q25
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2043	G36	Q25
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2045	G38	Q25
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2066	G59	Q25
2067	G60	Q25
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2069	G62	Q25
2070	G63	Q25
2071	G64	Q25
2072	G65	Q25
2073	G66	Q25
2074	G67	Q25
2075	G68	Q25
2076	G69	Q25
2077	G70	Q25
2078	G71	Q25
2079	G72	Q25
2080	G73	Q25
2081	G74	Q25
2082	G75	Q25
2083	G76	Q25
2084	G77	Q25
2085	G78	Q25
2086	G79	Q25
2087	G80	Q25
2088	G81	Q25
2089	G82	Q25
2090	G83	Q25
2091	G84	Q25
2092	G85	Q25
2093	G86	Q25
2094	G87	Q25

Examples 2095-2442 : The procedure is as in Examples 7-9, but the following compounds of formula $[G^+] \cdot [X^{m-}]_p \cdot [Y^{n+}]_q$ (XI), which can be prepared analogously to Examples 1-6, are used:

Ex.	G^+	X^{m-}	p	Y^{n+}	q
2095	G1	Q1	½		0
2096	G2	Q1	½		0
2097	G3	Q1	½		0
2098	G4	Q1	½		0
2099	G5	Q1	½		0
2100	G6	Q1	½		0
2101	G7	Q1	½		0
2102	G8	Q1	½		0
2103	G9	Q1	½		0
2104	G10	Q1	½		0
2105	G11	Q1	½		0
2106	G12	Q1	½		0
2107	G13	Q1	½		0
2108	G14	Q1	½		0
2109	G15	Q1	½		0
2110	G16	Q1	½		0
2111	G17	Q1	½		0
2112	G18	Q1	½		0
2113	G19	Q1	½		0
2114	G20	Q1	½		0
2115	G21	Q1	½		0
2116	G22	Q1	½		0
2117	G23	Q1	½		0
2118	G24	Q1	½		0
2119	G25	Q1	½		0
2120	G26	Q1	½		0
2121	G27	Q1	½		0
2122	G28	Q1	½		0
2123	G29	Q1	½		0
2124	G30	Q1	½		0
2125	G31	Q1	½		0
2126	G32	Q1	½		0
2127	G33	Q1	½		0
2128	G34	Q1	½		0
2129	G35	Q1	½		0
2130	G36	Q1	½		0
2131	G37	Q1	½		0
2132	G38	Q1	½		0
2133	G39	Q1	½		0
2134	G40	Q1	½		0
2135	G41	Q1	½		0
2136	G42	Q1	½		0
2137	G43	Q1	½		0
2138	G44	Q1	½		0
2139	G45	Q1	½		0
2140	G46	Q1	½		0
2141	G47	Q1	½		0
2142	G48	Q1	½		0
2143	G49	Q1	½		0
2144	G50	Q1	½		0
2145	G51	Q1	½		0
2146	G52	Q1	½		0
2147	G53	Q1	½		0
2148	G54	Q1	½		0
2149	G55	Q1	½		0
2150	G56	Q1	½		0
2151	G57	Q1	½		0
2152	G58	Q1	½		0
2153	G59	Q1	½		0
2154	G60	Q1	½		0
2155	G61	Q1	½		0
2156	G62	Q1	½		0
2157	G63	Q1	½		0
2158	G64	Q1	½		0
2159	G65	Q1	½		0
2160	G66	Q1	½		0
2161	G67	Q1	½		0
2162	G68	Q1	½		0
2163	G69	Q1	½		0
2164	G70	Q1	½		0
2165	G71	Q1	½		0
2166	G72	Q1	½		0
2167	G73	Q1	½		0

2168	G74	Q1	½		0
2169	G75	Q1	½		0
2170	G76	Q1	½		0
2171	G77	Q1	½		0
2172	G78	Q1	½		0
2173	G79	Q1	½		0
2174	G80	Q1	½		0
2175	G81	Q1	½		0
2176	G82	Q1	½		0
2177	G83	Q1	½		0
2178	G84	Q1	½		0
2179	G85	Q1	½		0
2180	G86	Q1	½		0
2181	G87	Q1	½		0
2182	G1	Q26	½		0
2183	G2	Q26	½		0
2184	G3	Q26	½		0
2185	G4	Q26	½		0
2186	G5	Q26	½		0
2187	G6	Q26	½		0
2188	G7	Q26	½		0
2189	G8	Q26	½		0
2190	G9	Q26	½		0
2191	G10	Q26	½		0
2192	G11	Q26	½		0
2193	G12	Q26	½		0
2194	G13	Q26	½		0
2195	G14	Q26	½		0
2196	G15	Q26	½		0
2197	G16	Q26	½		0
2198	G17	Q26	½		0
2199	G18	Q26	½		0
2200	G19	Q26	½		0
2201	G20	Q26	½		0
2202	G21	Q26	½		0
2203	G22	Q26	½		0
2204	G23	Q26	½		0
2205	G24	Q26	½		0
2206	G25	Q26	½		0
2207	G26	Q26	½		0
2208	G27	Q26	½		0
2209	G28	Q26	½		0
2210	G29	Q26	½		0

2211	G30	Q26	½		0
2212	G31	Q26	½		0
2213	G32	Q26	½		0
2214	G33	Q26	½		0
2215	G34	Q26	½		0
2216	G35	Q26	½		0
2217	G36	Q26	½		0
2218	G37	Q26	½		0
2219	G38	Q26	½		0
2220	G39	Q26	½		0
2221	G40	Q26	½		0
2222	G41	Q26	½		0
2223	G42	Q26	½		0
2224	G43	Q26	½		0
2225	G44	Q26	½		0
2226	G45	Q26	½		0
2227	G46	Q26	½		0
2228	G47	Q26	½		0
2229	G48	Q26	½		0
2230	G49	Q26	½		0
2231	G50	Q26	½		0
2232	G51	Q26	½		0
2233	G52	Q26	½		0
2234	G53	Q26	½		0
2235	G54	Q26	½		0
2236	G55	Q26	½		0
2237	G56	Q26	½		0
2238	G57	Q26	½		0
2239	G58	Q26	½		0
2240	G59	Q26	½		0
2241	G60	Q26	½		0
2242	G61	Q26	½		0
2243	G62	Q26	½		0
2244	G63	Q26	½		0
2245	G64	Q26	½		0
2246	G65	Q26	½		0
2247	G66	Q26	½		0
2248	G67	Q26	½		0
2249	G68	Q26	½		0
2250	G69	Q26	½		0
2251	G70	Q26	½		0
2252	G71	Q26	½		0
2253	G72	Q26	½		0

2254	G73	Q26	½		0
2255	G74	Q26	½		0
2256	G75	Q26	½		0
2257	G76	Q26	½		0
2258	G77	Q26	½		0
2259	G78	Q26	½		0
2260	G79	Q26	½		0
2261	G80	Q26	½		0
2262	G81	Q26	½		0
2263	G82	Q26	½		0
2264	G83	Q26	½		0
2265	G84	Q26	½		0
2266	G85	Q26	½		0
2267	G86	Q26	½		0
2268	G87	Q26	½		0
2269	G1	Q1	1	NH_4^+	1
2270	G2	Q1	1	NH_4^+	1
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2272	G4	Q1	1	NH_4^+	1
2273	G5	Q1	1	NH_4^+	1
2274	G6	Q1	1	NH_4^+	1
2275	G7	Q1	1	NH_4^+	1
2276	G8	Q1	1	NH_4^+	1
2277	G9	Q1	1	NH_4^+	1
2278	G10	Q1	1	NH_4^+	1
2279	G11	Q1	1	NH_4^+	1
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2281	G13	Q1	1	NH_4^+	1
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2287	G19	Q1	1	NH_4^+	1
2288	G20	Q1	1	NH_4^+	1
2289	G21	Q1	1	NH_4^+	1
2290	G22	Q1	1	NH_4^+	1
2291	G23	Q1	1	NH_4^+	1
2292	G24	Q1	1	NH_4^+	1
2293	G25	Q1	1	NH_4^+	1
2294	G26	Q1	1	NH_4^+	1
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2310	G42	Q1	1	NH_4^+	1
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2313	G45	Q1	1	NH_4^+	1
2314	G46	Q1	1	NH_4^+	1
2315	G47	Q1	1	NH_4^+	1
2316	G48	Q1	1	NH_4^+	1
2317	G49	Q1	1	NH_4^+	1
2318	G50	Q1	1	NH_4^+	1
2319	G51	Q1	1	NH_4^+	1
2320	G52	Q1	1	NH_4^+	1
2321	G53	Q1	1	NH_4^+	1
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2327	G59	Q1	1	NH_4^+	1
2328	G60	Q1	1	NH_4^+	1
2329	G61	Q1	1	NH_4^+	1
2330	G62	Q1	1	NH_4^+	1
2331	G63	Q1	1	NH_4^+	1
2332	G64	Q1	1	NH_4^+	1
2333	G65	Q1	1	NH_4^+	1
2334	G66	Q1	1	NH_4^+	1
2335	G67	Q1	1	NH_4^+	1
2336	G68	Q1	1	NH_4^+	1
2337	G69	Q1	1	NH_4^+	1
2338	G70	Q1	1	NH_4^+	1
2339	G71	Q1	1	NH_4^+	1

2340	G72	Q1	1	NH_4^+	1
2341	G73	Q1	1	NH_4^+	1
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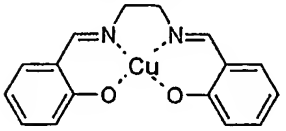
2343	G75	Q1	1	NH_4^+	1
2344	G76	Q1	1	NH_4^+	1
2345	G77	Q1	1	NH_4^+	1
2346	G78	Q1	1	NH_4^+	1
2347	G79	Q1	1	NH_4^+	1
2348	G80	Q1	1	NH_4^+	1
2349	G81	Q1	1	NH_4^+	1
2350	G82	Q1	1	NH_4^+	1
2351	G83	Q1	1	NH_4^+	1
2352	G84	Q1	1	NH_4^+	1
2353	G85	Q1	1	NH_4^+	1
2354	G86	Q1	1	NH_4^+	1
2355	G87	Q1	1	NH_4^+	1
2356	G1	Q26	1	NH_4^+	1
2357	G2	Q26	1	NH_4^+	1
2358	G3	Q26	1	NH_4^+	1
2359	G4	Q26	1	NH_4^+	1
2360	G5	Q26	1	NH_4^+	1
2361	G6	Q26	1	NH_4^+	1
2362	G7	Q26	1	NH_4^+	1
2363	G8	Q26	1	NH_4^+	1
2364	G9	Q26	1	NH_4^+	1
2365	G10	Q26	1	NH_4^+	1
2366	G11	Q26	1	NH_4^+	1
2367	G12	Q26	1	NH_4^+	1
2368	G13	Q26	1	NH_4^+	1
2369	G14	Q26	1	NH_4^+	1
2370	G15	Q26	1	NH_4^+	1
2371	G16	Q26	1	NH_4^+	1
2372	G17	Q26	1	NH_4^+	1
2373	G18	Q26	1	NH_4^+	1
2374	G19	Q26	1	NH_4^+	1
2375	G20	Q26	1	NH_4^+	1
2376	G21	Q26	1	NH_4^+	1
2377	G22	Q26	1	NH_4^+	1
2378	G23	Q26	1	NH_4^+	1
2379	G24	Q26	1	NH_4^+	1
2380	G25	Q26	1	NH_4^+	1
2381	G26	Q26	1	NH_4^+	1
2382	G27	Q26	1	NH_4^+	1

2383	G28	Q26	1	NH_4^+	1
2384	G29	Q26	1	NH_4^+	1
2385	G30	Q26	1	NH_4^+	1
2386	G31	Q26	1	NH_4^+	1
2387	G32	Q26	1	NH_4^+	1
2388	G33	Q26	1	NH_4^+	1
2389	G34	Q26	1	NH_4^+	1
2390	G35	Q26	1	NH_4^+	1
2391	G36	Q26	1	NH_4^+	1
2392	G37	Q26	1	NH_4^+	1
2393	G38	Q26	1	NH_4^+	1
2394	G39	Q26	1	NH_4^+	1
2395	G40	Q26	1	NH_4^+	1
2396	G41	Q26	1	NH_4^+	1
2397	G42	Q26	1	NH_4^+	1
2398	G43	Q26	1	NH_4^+	1
2399	G44	Q26	1	NH_4^+	1
2400	G45	Q26	1	NH_4^+	1
2401	G46	Q26	1	NH_4^+	1
2402	G47	Q26	1	NH_4^+	1
2403	G48	Q26	1	NH_4^+	1
2404	G49	Q26	1	NH_4^+	1
2405	G50	Q26	1	NH_4^+	1
2406	G51	Q26	1	NH_4^+	1
2407	G52	Q26	1	NH_4^+	1
2408	G53	Q26	1	NH_4^+	1
2409	G54	Q26	1	NH_4^+	1
2410	G55	Q26	1	NH_4^+	1
2411	G56	Q26	1	NH_4^+	1
2412	G57	Q26	1	NH_4^+	1
2413	G58	Q26	1	NH_4^+	1
2414	G59	Q26	1	NH_4^+	1
2415	G60	Q26	1	NH_4^+	1
2416	G61	Q26	1	NH_4^+	1
2417	G62	Q26	1	NH_4^+	1
2418	G63	Q26	1	NH_4^+	1
2419	G64	Q26	1	NH_4^+	1
2420	G65	Q26	1	NH_4^+	1
2421	G66	Q26	1	NH_4^+	1
2422	G67	Q26	1	NH_4^+	1
2423	G68	Q26	1	NH_4^+	1
2424	G69	Q26	1	NH_4^+	1
2425	G70	Q26	1	NH_4^+	1

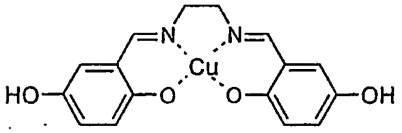
2426	G71	Q26	1	NH_4^+	1
2427	G72	Q26	1	NH_4^+	1
2428	G73	Q26	1	NH_4^+	1
2429	G74	Q26	1	NH_4^+	1
2430	G75	Q26	1	NH_4^+	1
2431	G76	Q26	1	NH_4^+	1
2432	G77	Q26	1	NH_4^+	1
2433	G78	Q26	1	NH_4^+	1
2434	G79	Q26	1	NH_4^+	1

2435	G80	Q26	1	NH_4^+	1
2436	G81	Q26	1	NH_4^+	1
2437	G82	Q26	1	NH_4^+	1
2438	G83	Q26	1	NH_4^+	1
2439	G84	Q26	1	NH_4^+	1
2440	G85	Q26	1	NH_4^+	1
2441	G86	Q26	1	NH_4^+	1
2442	G87	Q26	1	NH_4^+	1

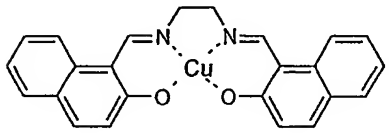
Example 2443 : The procedure is as in Examples 7-9, but the product of formula G89 according to Example 4 is used together with 20% by weight (based on the product according to Example G89) of the product of formula



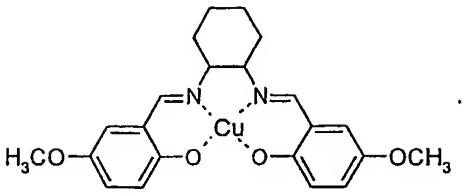
Example 2444 : The procedure is as in Example 2443, but the product of formula G89 according to Example 4 is used together with 20% by weight (based on the product according to Example G89) of the product of formula



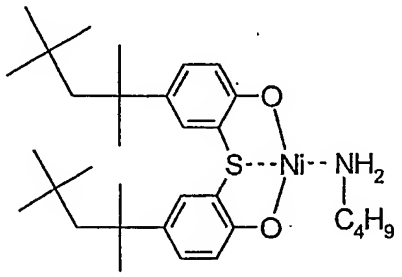
Example 2445 : The procedure is as in Example 2443, but the product of formula G89 according to Example 4 is used together with 20% by weight (based on the product according to Example G89) of the product of formula



Example 2446 : The procedure is as in Example 2443, but the product of formula G89 according to Example 4 is used together with 20% by weight (based on the product according to Example G89) of the product of formula

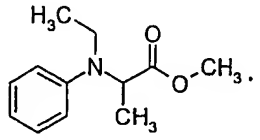


Example 2447 : The procedure is as in Example 2443, but the product of formula G89 according to Example 4 is used together with 20% by weight (based on the product according to Example G89) of the product of formula



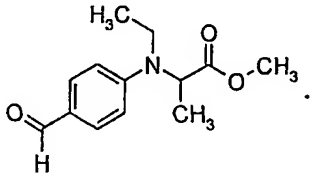
Examples 2448-2452 : The procedure is as in Examples 2443-2447, but the product of formula G90 according to Example 5 is used instead of the product of formula G89 according to Example 4.

Example 2453 : 12.1 g of N-ethylaniline are stirred in 22 ml of 2-chloro-propionic acid ethyl ester in the presence of 10.6 ml of sodium carbonate and 0.2 g of potassium iodide until the N-ethylaniline can no longer be detected in thin-layer chromatography. The chloropropionic acid ester is distilled off, and the oil that remains is taken up in ethyl acetate and extracted with water until salt-free. The dried organic phase is concentrated, yielding 20 g of an oily mass of formula:

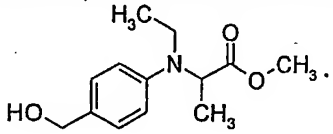


Example 2454 : 7.1 g of the compound according to Example 2453 are introduced into 20 ml of N,N-dimethylformamide and cooled in an ice bath. 3.2 ml of phosphorus oxytrichloride are then slowly added dropwise and the mixture is stirred first at 20°C, and then for a further 4 hours at 60°C. The cooled reaction mass is discharged into a small amount of ice-water and

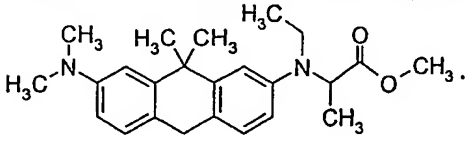
neutralised with dilute sodium hydroxide solution. The resulting oil is taken up in ethyl acetate and washed with sodium chloride solution. The organic phase is dried and concentrated, yielding 6.7 g of the product of formula:



Example 2455 : 6.7 g of the compound according to Example 2454 are dissolved in 50 ml of methanol, and 0.43 g of sodium borohydride is added. After 30 minutes at 20°C, the starting material can no longer be detected. The reaction solution is freed of methanol by distillation and the residue is taken up in ethyl acetate and washed with concentrated sodium chloride solution. The dried ethyl acetate phase is concentrated by evaporation; yielding 4.6 g of an oil of formula

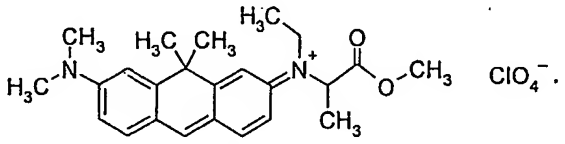


Example 2456 : 4.25 g of the compound according to Example 2455 are dissolved in 25 ml of dichloromethane, and 2.6 ml of 3-isopropenyl-N,N-dimethylaniline are added. While cooling with an ice bath, 16 ml of a 1M boron trichloride solution in dichloromethane are added and the mixture is left to react overnight in the initial ice-bath to complete the reaction. Then, while cooling in an ice bath, 16 ml of concentrated sulfuric acid are added dropwise. The resulting reaction mixture is discharged onto ice, neutralised with sodium hydroxide solution and taken up in dichloromethane. After being washed, the organic phase is dried and the dichloromethane is distilled off, leaving behind 5.8 g of a blue-green, very oxygen-senstive oil of formula

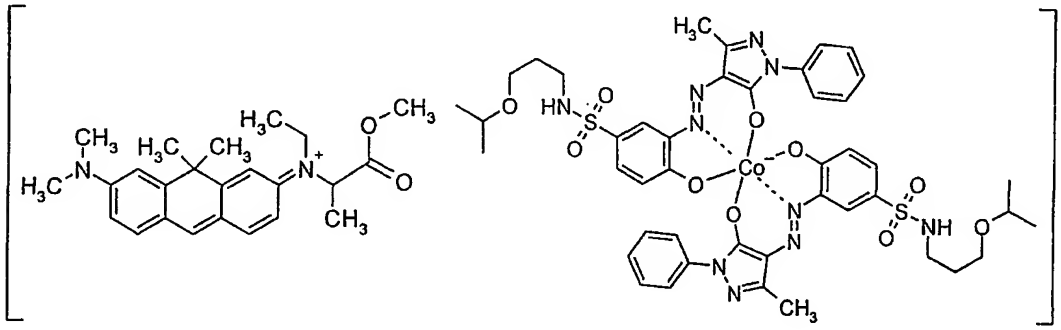


Example 2457 : 5.8 g of the compound according to Example 2456 are dissolved in 40 ml of 100% acetic acid, and 150 drops of 60% perchloric acid are added. 1.65 g of tetrabutylammonium (meta)periodate are added to the resulting mixture. Stirring is carried out for 3 hours at 40°C, and the reaction

mass is discharged into 250 ml of water and 25 g of sodium perchlorate monohydrate and the oily mass obtained is treated with a potassium perchlorate solution. After working up, 3.4 g of crude product are obtained. Repeated chromatographic purification of the crude product yields the analytically pure compound of the following formula:

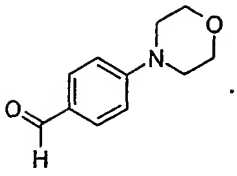


Example 2458 : 1.33 g of analytically pure product according to Example 2457 are dissolved in acetone with 2.78 g of the cobalt complex of structure Q20 and the solution is concentrated by evaporation. The residue is taken up in methylene chloride, extracted by shaking repeatedly with deionised water and, without drying of the organic phase, concentrated to dryness without residue, yielding 3.13 g of compound of formula:

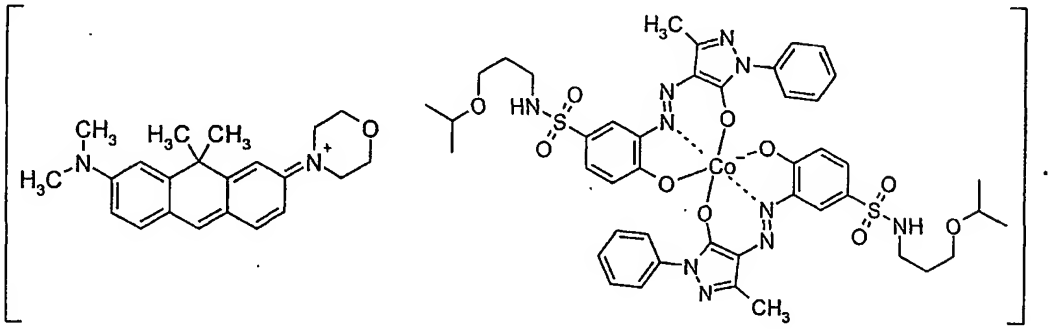


Example 2459: The procedure is as in Example 7, but instead of the product according to Example 1 there is used an equal amount of the product according to Example 2458. The absorption maximum of a recording support produced analogously to Example 7 is at 623 nm.

Example 2460 : 2.7 g of 4-fluorobenzaldehyde are stirred at 110°C in 20 ml of dimethyl sulfoxide with 3.74 g of morpholine and 3 g of potassium carbonate for 6 hours. Customary working-up yields 0.95 g of crystalline product of formula



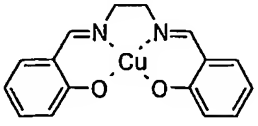
That product is processed further analogously to Examples 2455 to 2458; yielding the compound of formula:



Example 2461 : The procedure is as in Example 7, but instead of the product according to Example 1 there is used an equal amount of the product according to Example 2460. The absorption maximum of a recording support produced analogously to Example 7 is at 626 nm.

Example 2462 : The procedure is as in Example 7, but instead of the product according to Example 1 there is used an equal amount of the product according to Example 3. The absorption maximum of the recording support is at 625 nm.

Example 2463 : The procedure is as in Example 3, but instead of the metal complex of formula Q20 there is used an equimolar amount of the metal complex of formula Q16. The absorption maximum of a recording support produced analogously to Example 7 is at 631 nm.

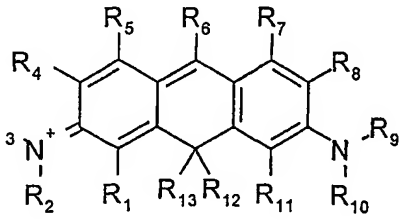
Example 2464 : The procedure is as in Example 1, but instead of the sodium salt of the metal complex of formula Q20 there is used the same amount of the product of formula  . The absorption maximum of a recording support analogous to Example 7 is at about 630 nm.

Examples 2465-2470 : Analogously to Example 7, recording supports are produced using the products of other Examples. The following absorption maxima are obtained:

Example	Recording support comprising product according to Example:	Absorption maximum
2465	98	623 nm
2466	183	636 nm
2467	1227	632 nm
2468	1576	621 nm
2469	1583	625 nm
2470	1921	633 nm

What is claimed is:

1. An optical recording medium, comprising a substrate and a recording layer, wherein the recording layer comprises a compound of formula (I)



$(X^{m-})_p$

$(Y^{n+})_q$ (I)

wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12} and R_{13} are each independently of the others hydrogen, G_1, or C_1-C_{24}alkyl, C_2-C_{24}alkenyl, C_2-C_{24}alkynyl, C_3-C_{24}cycloalkyl, C_3-C_{24}cycloalkenyl, C_7-C_{24}aralkyl, C_6-C_{24}aryl, C_4-C_{12}heteroaryl or C_1-C_{12}heterocycloalkyl, each unsubstituted or substituted by one or more identical or different substituents G_1,

wherein R_1 and R_2, R_1 and R_{13}, R_2 and R_3, R_3 and R_4, R_4 and R_5, R_5 and R_6, R_6 and R_7, R_7 and R_8, R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, R_{11} and R_{12} and/or R_{12} and R_{13} can independently of one another be bonded to one another in pairs separately or, when they contain substitutable sites, *via* a direct bond or *via* a $-CH_2-$, $-O-$, $-S-$, $-NH-$ or $-NC_1$-C_{24}alkyl- bridge in such a manner that, together with the atoms and bonds indicated in formula (I), five- or six-membered, saturated, unsaturated or aromatic, unsubstituted or G_1-substituted rings are formed,

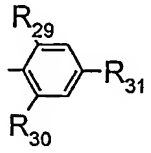
G_1 is any desired substituent,

X^{m-} is an inorganic, organic or organometallic anion,

Y^{n+} is a proton or a metal, ammonium or phosphonium cation, and

m and n are each independently of the other a number from 1 to 5, and p and q are each independently of the other 0 or a number from 0.2 to 6, the ratio of p and q to one another, depending upon m and n and, as applicable, the number of charged G_1, being such that in formula (I) there is no excess positive or negative charge.

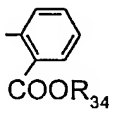
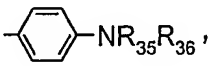
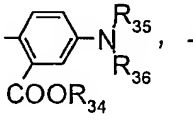
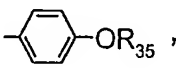
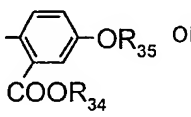
2. A recording medium according to claim 1, which additionally comprises a reflecting layer.

3. A recording medium according to claim 1 or 2, wherein R_6 is 

and R_{29}, R_{30} and R_{31} are each independently of the others hydrogen, halogen, $COOR_{32}$, OR_{32} or $NR_{32}R_{33}$, wherein R_{32} and R_{33} are each independently of the other hydrogen or C_1-C_{12}alkyl, C_2-C_{12}alkenyl, C_1-C_{12}cycloalkyl, C_2-C_{12}cycloalkenyl, C_6-C_{12}aryl or C_7-C_{13}aralkyl, each unsubstituted or substituted by one or two hydroxy substituents or by a metallocenyl or azo metal complex radical and uninterrupted or interrupted by 1, 2, 3, 4 or 5 oxygen and/or silicon atoms.

4. A recording medium according to claim 1, 2 or 3, wherein R_1, R_4, R_5, R_7, R_8 and R_{11} are hydrogen; R_2, R_3, R_9, R_{10}, R_{12} and R_{13} are each independently of the others methyl, ethyl or R_{14}, it being possible for R_2 and R_3, R_9 and R_{10}, R_{12} and R_{13} and/or R_9 and R_{10} also to be bonded together in pairs *via* a direct bond, methylene, -O- or -N(C_1-C_4alkyl); and R_6 is hydrogen or C_1-C_{12}alkyl, C_6-C_{12}aryl or C_7-C_{13}aralkyl, each unsubstituted or mono- to tetra-substituted by halogen, $-O^-$, $-OR_{26}$, -CN, $-NR_{26}R_{27}$, $-N^+R_{26}R_{27}R_{28}$, $-N(R_{26})COR_{27}$, $-COO^-$, $-COOR_{26}$, $-CONR_{26}R_{27}$, R_{14} or by $-N(R_{26})COR_{27}R_{28}$, wherein R_{26}, R_{27} and R_{28} are each independently of the others C_1-C_{12}alkyl, C_6-C_{12}aryl or C_7-C_{13}aralkyl.

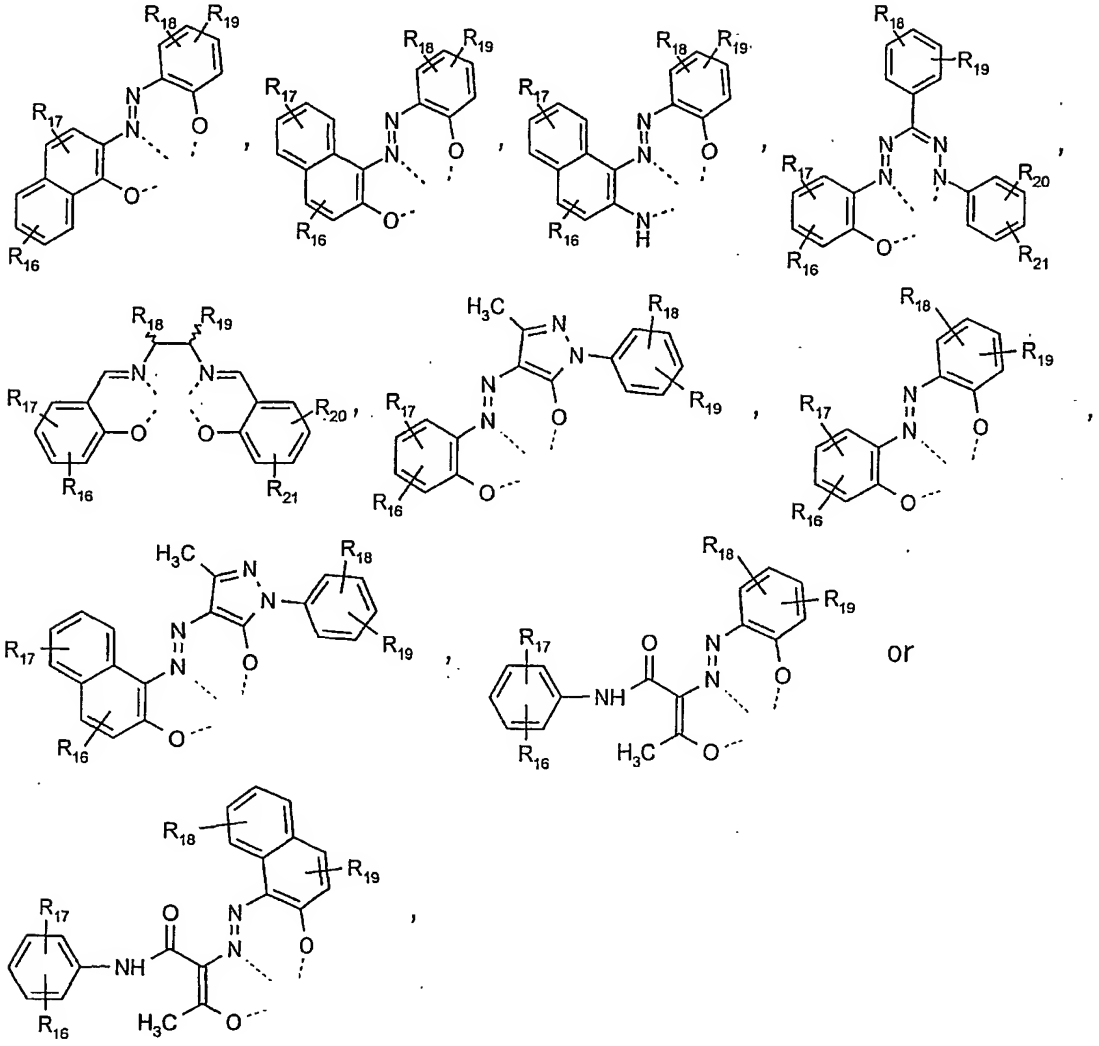
5. A recording medium according to claim 3 or 4, wherein R_6 is  ,

 ,  ,  ,  ,  or R_{37}, and

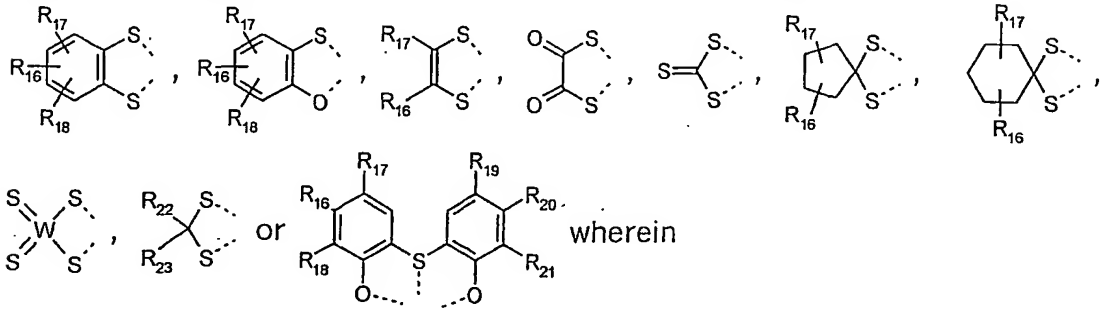
R_{34}, R_{35} and R_{36} are each independently of the others hydrogen or R_{37}, R_{37} being alkyl uninterrupted or interrupted by from 1 to 3 oxygen and/or silicon atoms and unsubstituted or substituted by one or two hydroxy substituents or by a metallocenyl or azo metal complex radical.

6. A recording medium according to claim 1, 2, 3, 4 or 5, wherein X^{m-} is a metal complex of formula $[(L_1)M_1(L_2)]^{m-}$ (III) or $[(L_3)M_2(L_4)]^-$ (IV), wherein M_1 and M_2 are a transition metal, preferably M_1 being Cr^{3+} or Co^{3+} and M_2 being

Ni^{2+}, Co^{2+} or Cu^{2+}, m is a number from 1 to 6, L_1 and L_2 are each independently of the other a ligand of formula



and L_3 and L_4 are each independently of the other a ligand of formula



wherein

R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21} are each independently of the others hydrogen, halogen, cyano, R_{24}, NO_2, $NR_{24}R_{25}$, NHCO-R_{24}, $NHCOOR_{24}$, SO_2–R_{24}, SO_2NH_2, SO_2NHR_{24}, $SO_2NR_{24}R_{25}$, SO_3^- or SO_3H, preferably hydrogen, chlorine, SO_2NH_2 or SO_2NHR_{24}, and R_{22} and R_{23} are each independently of the others CN, $CONH_2$, $CONHR_{24}$, $CONR_{24}R_{25}$, $COOR_{24}$ or COR_{24}, wherein R_{24} and R_{25} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}alkoxy-C_2-C_{12}alkyl, C_7-C_{12}aralkyl or C_6-C_{12}aryl, preferably C_1-C_4alkyl, each unsubstituted or substituted by hydroxy, halogen, sulfato, C_1-C_6alkoxy, C_1-C_6alkylthio, C_1-C_6alkylamino or by di-C_1-C_6alkylamino, or R_{24} and R_{25} together are C_4-C_{10}heterocycloalkyl; it also being possible for R_{16} and R_{17}, R_{18} and R_{19}, and/or R_{20} and R_{21} to be bonded together in pairs in such a manner that a 5- or 6-membered ring is formed.

7. A recording medium according to claim 1, 2, 3, 4 or 5, wherein Y^{n+} is $[NH_2R_{38}R_{39}]^+$, R_{38} being hydrogen or C_1-C_{12}alkyl and R_{39} being C_1-C_{24}alkyl or C_7-C_{24}aralkyl, and R_{38} and R_{39} together having from 8 to 25 carbon atoms.

8. A recording medium according to claim 1, 2, 3, 4 or 5, wherein m and n are each the number 1, p is a number from 1 to 2½, and q is a number from 0 to 1½, the sum of positive charges in formula (I) or (II) being equal to the sum of negative charges.

9. A recording medium according to claim 1, 2, 3, 4 or 5, wherein the dye of formula (I) has an absorption maximum at from 540 to 640 nm in ethanolic solution and a refractive index of from 2.0 to 3.0 in the range of from 600 to 700 nm in the solid.

10. A recording medium according to claim 1, 2, 3, 4 or 5, wherein the substrate has a transparency of at least 90% and a thickness of from 0.01 to 10 mm, preferably from 0.1 to 5 mm.

11. A recording medium according to claim 1, 2, 3, 4 or 5, wherein the reflecting layer consists of aluminium, silver, copper, gold or an alloy thereof and has a reflectivity of at least 45% and thickness of from 10 to 150 nm.

12. A recording medium according to claim 1, 2, 3, 4 or 5, wherein the recording layer is located between the transparent substrate and the reflecting layer and has a thickness of from 10 to 1000 nm, preferably from 30 to

300 nm, especially from 60 to 120 nm..

13. A recording medium according to claim 1, 2, 3, 4 or 5, the uppermost layer of which is provided with an additional protective layer having a thickness of from 0.1 to 1000 μm, preferably from 0.1 to 50 μm, especially from 0.5 to 15 μm, to which there may be applied a second substrate layer that is preferably from 0.1 to 5 mm thick and consists of the same material as the support substrate.

14. A recording medium according to claim 1, 2, 3, 4 or 5, which has a reflectivity of at least 15%.

15. A recording medium according to claim 1, 2, 3, 4 or 5, wherein between the recording layer and the reflecting layer and/or between the recording layer and the substrate there is additionally arranged at least one interference layer consisting of a dielectric material.

16. A method for the optical recording, storage and playback of information, wherein a recording medium according to any one of claims 1 to 15 is used.

17. A method according to claim 16, wherein the recording and the playback take place in a wavelength range of from 600 to 700 nm.

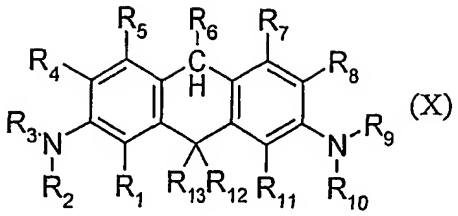
18. A process for the production of an optical recording medium, wherein a solution of a compound of formula (I) according to any one of claims 1 to 15 in an organic solvent is applied to a substrate having pits.

19. A process according to claim 18, wherein the application is carried out by means of spin-coating.

20. A compound of formula (I) according to claim 1, provided it is not known at the priority date of this Application.

21. Use of a compound of formula (I) according to claim 20 in the production of an optical recording medium.

22. A process for the preparation of a compound of formula (I) according to claim 1, wherein a compound of structure



(X)

is oxidised in the presence of a C_1-C_{18}carboxylic acid.

23. A process according to claim 22, wherein (meta)periodate is used as oxidising agent.

24. Use of a compound of formula (I) prepared according to claim 22 in the production of an optical recording medium.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/07434

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G11B7/24 C07C251/20 C07D231/38 C09B11/02 C09D11/18
C09B11/18 C09B11/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G11B C07C C07D C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 301 145 A (A INOUE) 5 April 1994 (1994-04-05) column 5, line 48; claim 1 column 2, line 45	1
A	EP 0 295 145 A (CANON) 14 December 1988 (1988-12-14) page 7, line 15 - line 16; claims 1,12 page 7, line 38 page 8, line 38 page 8, line 42	1
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 01, 30 January 1998 (1998-01-30). & JP 09 226250 A (HITACHI), 2 September 1997 (1997-09-02) abstract	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 November 2002	21/11/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Vanhecke, H

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/07434

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 851 621 A (H WOLLEB) 22 December 1998 (1998-12-22) cited in the application claims 1-23	1
X	US 3 781 711 A (K DREXHAGE) 25 December 1973 (1973-12-25) cited in the application column 6, line 1 - line 10; claims 1,3,7	20
X	DE 199 19 119 A (DREXHAGE) 2 November 2000 (2000-11-02) cited in the application claims 1-19	20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 02/07434

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 20,22,23
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 20,22,23

Present claims 20,22 and 23 relate to an extremely large number of possible compounds and methods. In fact, the claims contain so many options that a lack of clarity (and/or conciseness) within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear namely: those compounds comprising a metal complexing anion as recited in the examples

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/07434

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5301145	A	05-04-1994	JP	1019532 A	23-01-1989
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DE 19919119	A	02-11-2000	DE	19919119 A1	02-11-2000
			AU	4297100 A	10-11-2000
			WO	0064986 A1	02-11-2000
			EP	1173519 A1	23-01-2002